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CHEMICAL PROPERTIES AND METHODS OF ANALYSIS
OF REFRACTORY COMPOUNDS

G.V. Samsonov et al. Editors

Translation of "Khimicheskiye Svoystva
i Metody Analiza Tugoplavkikh Soyedi-
neniy". Kiev, Naukova Dumka Press,
1969, pp. 1-164

(NASA-TM-75335) CHEMICAL PROPERTIES AND
METHODS OF ANALYSIS OF REFRACTORY COMPOUNDS
(National Aeronautics and Space
Administration) 201 p HC A10/MF A01

N79-10166

CSCL 07D G3/25 36041
Unclas

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
LEWIS RESEARCH CENTER
OCTOBER 1978

ANNOTATION

This collection gives the results of studies on the chemical properties and original methods for analyzing refractory compounds and alloys based on them, which are used in various fields of new technology.

It is for the use of chemist-analysts, engineers, and workers in scientific-research institutes, plant laboratories, fellows, and students in advanced courses of chemistry and metallurgy.

TABLE OF CONTENTS

/161

Ye. Ye. Kotlyar and T. N. Nazaruchuk. Reactions of Group IV and V Transition Metal Carbides With Some Acids	1
M. I. Sokhor and G. V. Sofronov. Method for the Quantitative X-ray Analysis of the Free Carbon Concentration in Boron Carbide	9
L. A. Mashkovich and A. F. Kuteynikov. Method for Separating and Determining Free Carbon in Materials Containing Refractory Compounds.	20
L. Ye. Pechentkovskaya and T. N. Nazarchuk. The Stability of the Compounds of the Boron-Carbon System in Oxygen at High Temperatures	30
L. Ye. Pechentkovskaya and T. N. Nazarchuk. Chemical Properties of Boron Carbonitride	37
L. L. Vereykina. Oxidation of the Phosphides of Boron, Gallium and Indium in Air.	44
I. N. Godovannaya and O. I. Popova. Resistance of Refractory Materials Based on Silicon Nitride-Silicon Carbide to Oxidation at High Temperature	50
M. M. Antonova. Methods for Producing and The Chemical Stability of the Group IV and V Transition Metal Hydrides	54
A. A. Reshchikova and Z. S. Medvedeva. Chemical Analysis of the Products from the Reaction of Boron with Arsenic and Phosphorus.	64
L. N. Kugay and O. F. Galadzhly, and V. II. Kornilova. Complexometric Analysis of Molybdenum Alloys	75
G. T. Kabannik and O. I. Popova. Analysis of the Germanides of Titanium, Zirconium, Hafnium and Tantalum	84
O. I. Popova. Chemical Properties of the Germanides.	89
V. A. Obolonchik and T. M. Mikhlin. Analysis of the Selenides of the Rare Earth Elements	96
S. F. Boremskaya and G. T. Kabannik. Complexometric Analysis of Alloys of the Rare Earth Oxides with the Group II Oxides and Chromium Oxide.	100
L. V. Zaslavskaya, N. V. Ivanova, and N. F. Lashko. Separatio	

L. V. Zaslavskaya, N. V. Ivanova, and N. F. Lashko. Separation of Alloyed Chromium Carbides of the Type Cr_2C (Metastable) and Cr_{23}C_6 or Cr_7C_3 Isolated from Steels and Alloys.	107
G. G. Georgiyeva, N. F. Lashko, and K. P. Sorokina. Chemical and Electrochemical Methods for the Separation of the MeC Carbides and $\text{Me}(\text{C},\text{N})$ Carbonitrides of the Group IV and V Metals	113
Ye. F. Yakoleva, I. M. Dubrovina, and L. V. Stegnukhina. Electrolytic Separation of the α -Phase from Heat Resistant Steels and the Determination of Its Composition.	120
A. P. Obukhov, V. N. Gurin, I. R. Kozlova, Z. P. Terent'eva, and T. I. Mazina. Reactions of the Refractory Group V Metals with Zinc.	126
Z. S. Mukhina, L. I. Ill'ina, and N. S. Kondurkova. Determination of Tungsten in Binary Tungsten- Molybdenum Alloys.	133
V. G. Shcherbakov, S. K. Stegendo and R. A. Antonova Determination of Molybdenum in the Presence of Tungsten.	140
Ye. I. Nikitina. Photometric Determination of Boron in Nickel and Titanium Borides Using the Magne- son I Reagent in an Alkaline Medium.	145
V. I. Kornilova. Spectrophotometric Study of the Re- actions of Compound Formation Between Niobium with the Pan Reagent	154
V. G. Shcherbakov and G. V. Onuchina. Determination of Arsenic in Very Pure Molybdenum	158
N. V. Vekshina and L. Ya. Markovskiy. Chemical Phase Analysis of Mixtures of Carbides, Borides and Borocarbides	163
L. Ya. Markovskiy, N. V. Vekshina and Ye. T. Bezruk. The Reaction of Borides with Carbon and Carbides	177
S. V. Radzikovskaya and V. F. Bukhanevich. Chemical Properties and Analysis of Some Transition Metal Sulfides	184
V. P. Kopylova and T. N. Nazarchuk. Analysis of the Silicides of the Group IV-VI Transition Metals	188

STANDARD TITLE PAGE

1. Report No. NASA TM-75335	2. Government Accession No.	3. Recipient's Catalog No.	
4. Title and Subtitle CHEMICAL PROPERTIES AND METHODS OF ANALYSIS OF REFRACTORY COMPOUNDS		5. Report Date OCTOBER 1978	
		6. Performing Organization Code	
7. Author(s) G.V. Samvohov, I.N. Frantsevich, V.N. Yermenko, T.N. Nazarchuk and O.I. Popova, Editors		8. Performing Organization Report No.	
9. Performing Organization Name and Address SCITRAN Box 5456 Santa Barbara, CA 93108		10. Work Unit No.	
		11. Contract or Grant No. NASW-3198	
12. Sponsoring Agency Name and Address National Aeronautics and Space Administration Washington, D.C. 20546		13. Type of Report and Period Covered Translation	
		14. Sponsoring Agency Code	
15. Supplementary Notes Translation of "Khimicheskiye Svoystva i Metody Analiza Tugoplavkikh. Soyedineniy." Kiev, Naukova Dumka Press, 1969, pp. 1-164 (A70-12177)			
16. Abstract			
17. Key Words (Selected by Author(s))		18. Distribution Statement Unclassified - Unlimited	
19. Security Classif. (of this report) Unclassified	20. Security Classif. (of this page) Unclassified	21. No. of Pages 203	22.

REACTION OF THE CARBIDES OF THE GROUP IV AND V TRANSITION METALS WITH SOME ACIDS

Ye. Ye. Kotlyar and T. N. Nazarchuk**

The reactions of the carbides of the Group IV and V transition metals with acids and bases have been studied to find qualitative or semiquantitative data on their chemical stability. No interest was given to the composition of the gaseous decomposition products [2].

The purpose of this work was to study the nature of the reaction between the carbides with phosphoric, sulfuric and nitric acids, to determine the composition of the gaseous decomposition products, and to try to use the resulting data to discuss the nature of the bonds in the carbides.

The reactions of the carbides with concentrated phosphoric, sulfuric, and nitric acid were studied in an inert gas atmosphere -- nitrogen -- with heating using the apparatus shown in Fig. 1.

The sample of the carbide, 0.1-0.3 g in weight, was placed in a Wurts flask and 30-40 ml of the acid was added. In studying the reactions of the carbides with sulfuric acid, 50 ml of 80% solution of isopropyl alcohol was poured into the first wash bottle to absorb the SO_3 [4]; 50 ml of a 2% solution of iodine was placed in the second wash bottle to absorb the SO_2 . In studying the reactions of the carbides with nitric acid, both bottles were filled with 1:1 sulfuric acid to absorb the nitrogen oxides. Then the entire system was connected as shown in Fig. 1.

Nitrogen was passed through the entire system slowly -- for two to two and a half hours -- (3-4 bubbles per second) to displace the

*Numbers in margin indicate pagination of original foreign text.

**Institute for Material Behavior Problems AN Ukr. SSR)

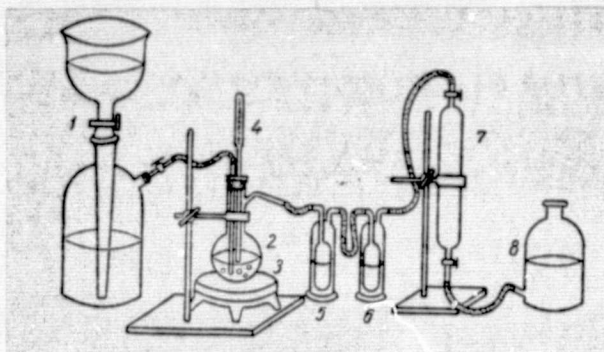


Fig. 1. Apparatus for studying the reactions between the carbides and acids:

1) gas meter with nitrogen; 2) Würtz flask; 3) electric heater; 4) thermometer; 5) bottle with 80% isopropyl alcohol for the absorption of SO_3 ; 6) bottle with the 2% iodine solution for absorbing SO_2 ; 7) gas burette; 8) pressure bottle.

air before the beginning of the reaction. After this, the reaction mixture was heated, leaving the stopcock in the gas burette open and the gases which were evolved were collected. After the reaction was finished, the solution was analyzed for the metal concentration and the insoluble residue was analyzed for the concentration of carbide and free carbon. The analysis of the gas mixture was done chromatographically. The material balance with respect to carbon was determined with an accuracy of 3-5%.

At 230-260°C, concentrated phosphoric acid ($d = 1.7$) decomposes only the zirconium and hafnium carbides. The decomposition begins at 230-240°C, and the dissolution goes rapidly at 250°. These carbides decompose completely upon boiling for 30-40 min. The titanium, vanadium, niobium, and tantalum carbides do not decompose in phosphoric acid even for heating to 300°C.

The main gaseous product from the reaction of the hafnium and zirconium carbides with phosphoric acid is methane (70-90% by volume). In addition to it, hydrogen (1-3%) and carbon dioxide are among the gaseous products (see Table 1).

TABLE 1

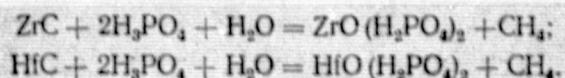
COMPOSITION OF THE PRODUCTS FROM THE REACTION OF THE GROUP IV AND V TRANSITION METAL CARBIDES WITH SULFURIC, PHOSPHORIC AND NITRIC ACIDS

Reaction Products	Reaction Temperature °C	Reaction Time hrs.	Amount of Carbide Decomposed %	Amorphous Carbon	Composition of Gas Mixture (Chromatographic method)			
					CH ₄	CO	CO ₂	H ₂
ZrC+H ₃ PO ₄ (d=1.7 g/cm ³)	260-270	1	100.0	—	91.4	—	7.8	0.8
	250-255	1	100.0	—	87.3	—	12.0	0.7
HfC+H ₃ PO ₄ (d=1.7 g/cm ³)	230-240	1.5	77.0	—	62.1	—	35.2	3.0
	250	1	100.0	—	77.2	—	19.3	3.4
	250-270	1.5	100.0	—	69.3	—	28.9	1.7
TiC+H ₂ SO ₄ (d=1.84 g/cm ³)	240-250	2	74.5	57.0	—	18.0	8.0	2.0
	250-270	2	76.0	33.0	—	6.3	92.4	1.3
	315-320	1	100.0	25.7	—	5.5	92.0	1.5
ZrC+H ₂ SO ₄ (d=1.84 g/cm ³)	260	1	100.0	14.2	48.2	—	48.2	3.0
	200-235	1.5	100.0	7.0	71.0	—	26.5	2.5
HfC+H ₂ SO ₄ (d=1.84 g/cm ³)	264-268	1	100.0	16.1	64.2	—	31.8	4.0
	290-300	1	100.0	6.3	16.2	—	81.3	2.4
VC+H ₂ SO ₄ (d=1.84 g/cm ³)	260	1.5	—	—	—	20.0	78.0	2.0
	300	1	—	—	—	—	96.4	3.6
NbC+H ₂ SO ₄	260	1.5-2	93.0	36.3	—	19.7	79.0	1.3
	280	1.5	92.0	47.0	—	24.3	73.8	1.9
	290-310	1	100.0	—	—	13.7	82.9	3.4
	265	1.5	81.0	13.0	—	5.4	92.3	2.3
TaC+H ₂ SO ₄	255	1.5	75.0	10.0	—	2.2	96.0	1.6
	276	1.0	80.0	6.0	—	6.0	92.3	1.7
ZrC+HNO ₃	110-120	0.5	100.0	—	Traces	—	95-97	2-3
HfC+HNO ₃	110-120	0.5	100.0	—	Same	—	95-97	2-3
NbC+HNO ₃ +NH ₄ F	110-120	0.5	100.0	—	—	Traces	95-97	2-3
TaC+HNO ₃ +NH ₄ F	110-120	0.5	100.0	—	—	Same	95-97	2-3

The resulting solutions are thick and transparent. For extensive dilution, white amorphous precipitates are formed which, after roasting, are converted into pyrophosphates with the composition $Zr_2P_2O_7$ and $Hf_2P_2O_7$. According to Brauer [5], the acid phosphates of zirconium and hafnium, $ZrO(H_2PO_4)_2$ and $HfO(H_2PO_4)_2$ are soluble in the freshly formed state, in a mixture of phosphoric, oxalic, and sulfuric acids, and form soluble complexes. Apparently these complexes are also formed in the presence of a large excess of concentrated phosphoric acid. Upon being diluted with water, i.e., with a decrease in the

concentration of the phosphoric acid, they are converted into the insoluble, intermediate phosphates, and they precipitate out.

The decomposition of the hafnium and zirconium carbides by phosphoric acid can be represented by the equations:



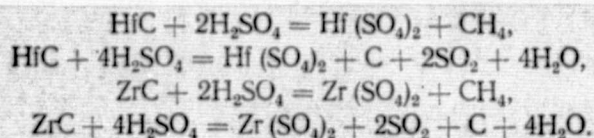
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Concentrated sulfuric acid decomposes all of the carbides at 200-300°C. The decomposition of the hafnium and zirconium carbides sets in at 200-220°C, and at 230-250°C they dissolve very rapidly and are completely decomposed in 30-40 min. The titanium, niobium, and tantalum carbides decompose to 70-80% upon boiling at 250-260°C for 1.5 hrs. They decompose completely for boiling for 1.5-2 hrs. at 290-310°C. The decomposition of all the carbides is accompanied by the formation of amorphous carbide which, in the finely divided state, gives the solution a brownish-black color. At the beginning of the interaction, clumps of amorphous carbon are observed in the solution and on the vessel's walls. Towards the end of the reaction, the solution clears up and at 290-310°C it becomes transparent. /5

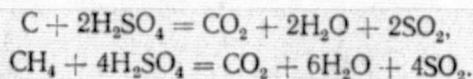
The formation of the amorphous carbon was observed by Greenwood and Osborne [6] in the reaction of lanthanum dicarbide with 4N sulfuric acid. The 2% iodine solution clears up markedly during the reaction and, in many cases, it is decolorized by the SO₂ that is evolved. /6

We can see from the data in the table that the reactions of the zirconium and hafnium carbides with sulfuric acid differ from the reactions of the titanium, vanadium, niobium and tantalum carbides because of the temperature range and length of time required for the dissolution and also in the composition of the gaseous products. The gaseous decomposition products from zirconium and hafnium carbides contain methane (50-70 volume %), CO₂ (30-50 volume %), and hydrogen (2.5-4.0 volume %). The ratio of the methane, carbon dioxide, and hydrogen depends on the temperature.

THE MAIN REACTIONS FOR THE DECOMPOSITION OF THE HAFNIUM AND ZIRCONIUM CARBIDES BY SULFURIC ACID CAN BE REPRESENTED BY THE EQUATIONS:



Secondary Reactions



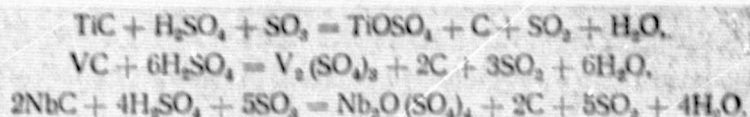
The reactions of the titanium, vanadium, niobium, and tantalum carbides with concentrated sulfuric acid take place with the formation of amorphous carbon. The amount of amorphous carbon in relation to all of the carbon in the titanium carbide which is decomposed at 240-270°C is equal to 33-57%; for niobium carbide, it is 47-36%. Vanadium carbide decomposes partially with the formation of vanadyl sulfate (green solution) and an insoluble yellow precipitate whose composition, according to the results of the analysis, corresponds to the formula $\text{V}_2(\text{SO}_4)_3$. In all the other cases, the solutions after the decomposition are thick and transparent, and no precipitates are formed upon dilution. Hydrolysis is only observed for the solutions after prolonged standing. From this, it follows that the titanium, niobium and tantalum carbides decompose with the formation of oxysulfates which are stable in concentrated sulfuric acid [1].

The following are present in the gaseous products: carbon monoxide (5-25%), carbon dioxide (70-90%) and hydrogen (1.5-3.0%). Methane was not observed in the gas phase in the given temperature range.

The ratio of the amorphous carbon, carbon monoxide and carbon dioxide depends on the temperature. Based on this, it may be assumed that CO and CO_2 are not the direct products from the carbide decom-

position, but are formed because of the oxidation of the amorphous carbon which is formed by the sulfuric acid.

The decomposition of the titanium, niobium and tantalum carbides with fuming sulfuric acid can be represented by the equations:

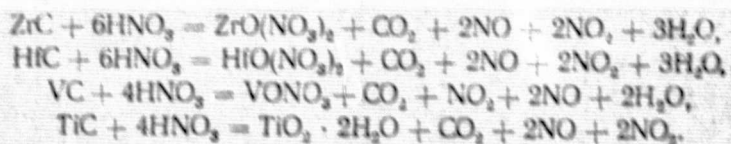


Nitric acid ($d = 1.43$) and 1:1 nitric acid decompose the carbides of zirconium, hafnium, titanium, and vanadium at 100-110°C. Carbon is not formed in the decomposition. After the dissolution of the vanadium, zirconium and hafnium carbides, the solutions are transparent, i.e., the reaction takes place with the formation of soluble nitrates. Titanium carbide decomposes completely with the formation of titanium hydroxide $\text{TiO}_2 \cdot n\text{H}_2\text{O}$.

For the decomposition of the zirconium and hafnium carbides, hydrogen (2-3%) and traces of methane are present along with carbon dioxide (95-97%) in the gas fraction. For the decomposition of the vanadium and titanium carbides, hydrogen (2-3%) and traces of carbon monoxide are present in the gaseous products along with carbon dioxide.

The niobium and tantalum carbides are decomposed by nitric acid in the presence of a 5% solution of ammonium fluoride at 100-120°C. After the decomposition, the solutions are transparent and no amorphous carbon is formed. The gaseous products contain carbon dioxide (96-97%) hydrogen (2-3%) and traces of carbon monoxide.

The reactions of the carbides with nitric acid take place according to the following equations:



It follows from the results that only zirconium and hafnium carbide are decomposed by phosphoric and sulfuric acids to form methane (as the main gaseous product), i.e., the carbon in these carbides is present in the form of the C^4 groups which have a stable sp^3 electron configuration. The even carbon bonds are symmetrical and identical and form polarcovalent bonds with the metal atoms, which results in a marked polarization of the ZrC and HfC molecules. Apparently, the ionic bond for these carbides is not predominant, since they are not decomposed by water and dilute acids like the ionic carbides, for example ScC , YC , etc. The absence of methane in the gaseous decomposition products from the decomposition of the titanium, vanadium, niobium and tantalum carbides indicates either that there is no ionic Me-C bond in these carbides or it is present to only a slight degree. /8

As we have shown, the carbides of the Group IV transition metals, particularly zirconium and hafnium, are much less chemically stable than the Group V carbides. In this case, the chemical stability of the Group IV carbides decreases as the atomic number of the transition metal increases, going from the titanium carbide to the hafnium carbide. This can be explained, as we showed above, by the increase in the amount of ionic bond in this series. The chemical stability of the Group V carbides, conversely, increases with an increase in the atomic number in going from vanadium carbide to tantalum carbide.

The tantalum carbide approaches the covalent carbides in its chemical stability. This is apparently explained by the fact that the covalent bonds between the atoms of the transition metals develop significantly in the Group V carbides. The amount of the covalent Me-Me bond increases with a decrease in the acceptor capacity of the metal going from the vanadium carbide to the tantalum carbide [3].

CONCLUSIONS

Concentrated phosphoric acid decomposes only the zirconium and hafnium carbides at $230-250^{\circ}C$ with the evolution of methane (70-90% by volume). The titanium, vanadium, niobium and tantalum carbides are not decomposed by phosphoric acid even at $300^{\circ}C$.

METHOD FOR THE QUANTITATIVE X-RAY ANALYSIS OF THE
FREE CARBON CONCENTRATION IN BORON CARBIDE

19

M. I. Sokhor and G. V. Sofronov*

At the present time the principal method for the quantitative determination of the concentration of free carbon in boron carbide is chemical analysis. Two chemical methods are known: the direct determination of C_{free} and from the data on B_{total} and C_{total} . The direct chemical analysis for C_{free} is based on treating the boron carbide with a chromic mixture and setting up the graph for the amount of CO_2 which is evolved as a function of the duration of oxidation. However, in treating the sample with the chromic mixture, the partial oxidation of the boron carbide phase takes place which may give elevated results for the chemical analysis for C_{free} . In addition, it is assumed in both methods that the boron carbide always has the same composition given by the formula B_4C and that the C_{free} is in fact free, pure carbon [5]. Because of the assumption that the composition of the carbon and boron carbide are constant, a second assumption follows that the properties of both phases are constant, particularly their oxidizability.

Meanwhile, no proof has been given that the properties of the carbon and the boron carbide are constant in different samples. Studies that have been made (1957-1961) show that often the free carbon in the boron carbide is not pure graphite but contains boron in the form of a solid solution of variable concentration. The boron carbide may have a wide range of compositions from B_4C to $\text{B}_{6.75}\text{C}$ [3,8].

These assumptions in the existing chemical methods for the quantitative determination of the C_{free} concentration in boron carbide made it necessary to develop a method for x-ray quantitative analysis for the free carbon in it, taking into account the composition and structure of the boron carbide and carbon phases [9].

The diffraction diagrams for single-phase samples of boron car-

*VNIIASH (All-Union Scientific-Research Institute of Abrasives and Grinding.

bide and graphite and for a sample of technical boron carbide, which contains free carbon, are shown in Fig. 1. The determination of the intensity of the (002) line for graphite and the relative intensity of the (110) line of boron carbide is the basis for developing the given x-ray method. These lines were selected because the amount of free carbon in technical boron carbide usually does not exceed a few percents and therefore the graphite phase will only be represented by a single, very strong line for graphite (002) with $\theta_{00} \approx 15^\circ$ in the x-ray diffraction diagrams and its intensity in such diagrams is close to the intensity for the neighboring line (110) for the boron carbide phase with $\theta_{00} \approx 18.5^\circ$ (Fig. 2).

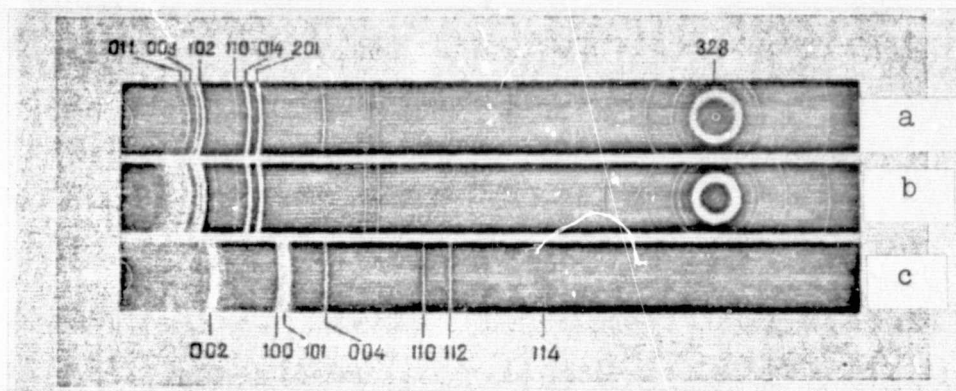


Fig. 1. X-ray diffraction diagram for a single phase boron carbide $B_{4.78}C$ (a), technical boron carbide containing boron carbide and about 2% free carbon (b), and ARV graphite (c). Radiation $Co = K_\alpha$.

The x-ray quantitative analysis for the C_{free} concentration in boron carbide was developed on the basis of the method of superposition suggested by Palatnik [4].

The superposition method is based on the comparison of x-ray diffraction diagrams for the system being analyzed with standard superposition diagrams obtained by recording the diffraction diagrams of the single phase substances, which are components of the two-phase system being analyzed, on a single film. By varying the ratio of the exposures for the individual components, the ratio of the line intensities can be changed on the superposition x-ray diagrams which is equivalent to changing the concentration of the components in the mixture. /11

It was necessary to develop and produce a special camera of the D-85 type to get the superposition x-ray diagrams. The camera was 85 mm in diameter and it allowed consecutive x-ray diagrams to be taken for two and more samples on a single film without recharging the camera [6]. The camera with the individual parts is shown in Fig. 3. In contrast to the usual Debye camera, the D-85 has a replaceable holder unit for the cylindrical sample, which allows the sample to be adjusted outside the camera by means of a special adjusting attachment (4). The holder with the adjusted sample is set in the charged camera. The camera allows the lines which correspond to reflection angles θ from 7 to 87.5° to be recorded [2]. Provision is made for the rotation of the sample during exposure.

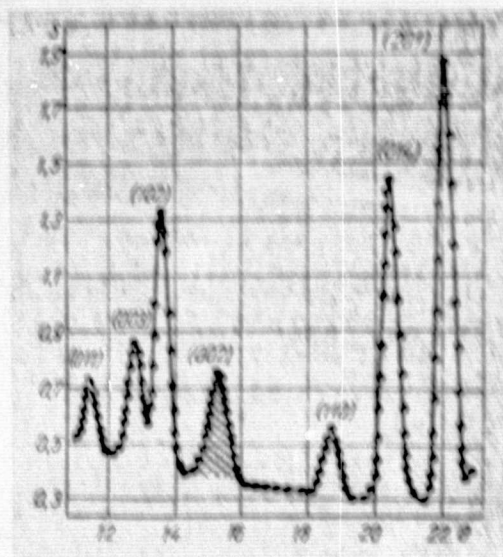


Fig. 2. Microphotogram of the front segment of the x-ray diagram for technical boron carbide containing free carbon (six front lines are given for boron carbide and the (002) line of graphite). Radiation $\text{Co} = K_\alpha$.

Various carbon materials have fine differences in the degree of development of the crystal lattice, the sample and dimensions of diagram (Fig. 5). Specifically, the fine structure and absolute intensity of the strongest line (002) changes as a function of the structural state of the carbon phase and this line was used to determine the concentration of C_{free} in the sample. The experimentally determined intensity of the (002) line for petroleum coke is shown as a function of the graphitizing temperature in Fig. 6. The intensity of the (002) line for ARV graphite is arbitrarily taken as 100%. We can see that as the temperature of graphitizing increases, the intensity of the (002) line for the petroleum coke increases. However, as we can see from the x-ray diagrams, the diffuseness and washing out of the edges of the (002) line for petroleum coke are retained. Clarity, sharpness, a high intensity and the absence of splitting for the (002) line are characteristic for ARV or Acheson graphites. Natural graphite

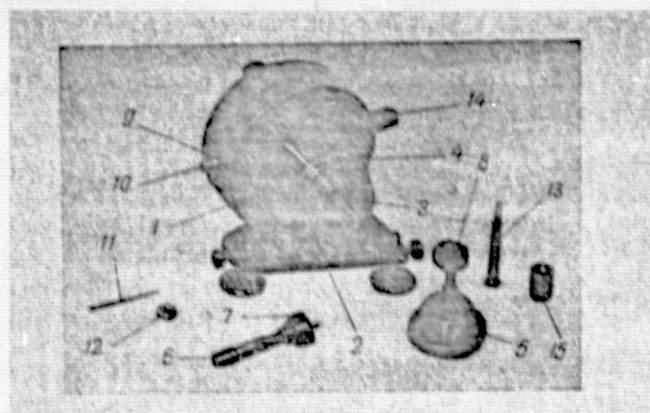


Fig. 3. The D-85 camera in unassembled form:

1) body; 2) block which connects the body with the main camera; 3) slide bearing in which the housing of the sample holder is placed; 4) the pulley which is attached to the bearing 3; 5) conical housing with the sample holder unit placed in it; 6) conical rod of the sample holder; 7) permanent magnet pressed onto the rod 6; 8) soft iron disk on which the sample is attached (the sample is adjusted by moving the disk with the magnet; 9) bushing which guides the collimator 10; 11) needle which goes into the collimator 10 and cuts off an x-ray beam 0.5-0.8 mm in diameter [7]; 12) nut for setting the filter and attaching the traps (it screws into the bushing 9; 13) trap for the primary beam; 14) bushing in which the trap 13 is set; 15) nut with a fluorescent screen (it screws into the bushing 14).

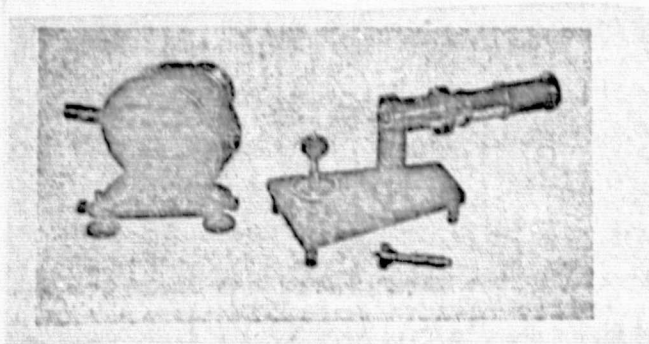


Fig. 4. The D-85 camera in the assembled state and the adjusting attachment which allows the sample to be adjusted outside the camera.

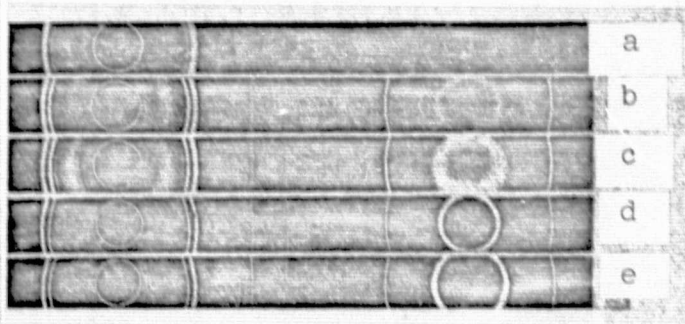


Fig. 5. X-ray diffraction diagrams for different carbon materials:

a) petroleum coke roasted at 1550°C for 1.5 hrs.; b) Acheson graphite; c) ARV graphite; d) natural graphite; e) graphite extracted from graphitized boron carbide. Chromium radiation.

gives a split (002) line which is due to the sample's texture.

Many years of practice in microscopic and x-ray diffraction studies in our institute (V. G. Kondakov and A. A. Kalinina) of different samples of technical boron carbide has shown that the structural state of the carbon phase in the boron carbide may be different, and it is determined by the technological conditions. In high quality boron carbide, the free carbon is present in the form of a finely dispersed phase which often forms a eutectic with the boron carbide and which is a solid solution of boron in graphite. Formally, this finely dispersed graphite in boron carbide can be compared, in terms of the x-ray diffraction, to a carbon material with a low degree of graphitization -- for example, petroleum coke roasted at 1550°C. We have encountered graphite in the form of larger segregations also /14 in the fusion products from technical boron carbide and quite often in hot pressed boron-carbon alloys. Such graphite gives an x-ray diffraction effect similar to that produced by ARV or Acheson graphite. In individual cases for boron-carbon alloys produced by repeated hot pressing or in graphitized fused boron carbide when the boron carbide decomposes, the graphite is segregated in the form of developed petal-crystals which form a texture in the preparation of the samples. The x-ray diagrams for such graphite are similar, with respect to the fine structure and intensity of the lines, to the x-ray diagrams for natural graphite (Fig. 5,e), although often the lattice periods a, and particularly c, are greater than for the natural graphite, which is apparently due to the dissolution of the boron which is formed from the decomposition of the boron carbide, in the graphite.

In obtaining a series of superposition diffraction diagrams, graphite ARV (0.05% moisture, 0.16% ash, and 0.95% volatile materials) and boron carbide having the composition $B_{4.78}C$ which, according to the results of chemical analysis, does not contain free carbon and which only gives lines of boron carbide on the x-ray diagram, were used as the main components.

The differences noted above in the structural state of the carbon phases in the various samples of technical boron carbon made it

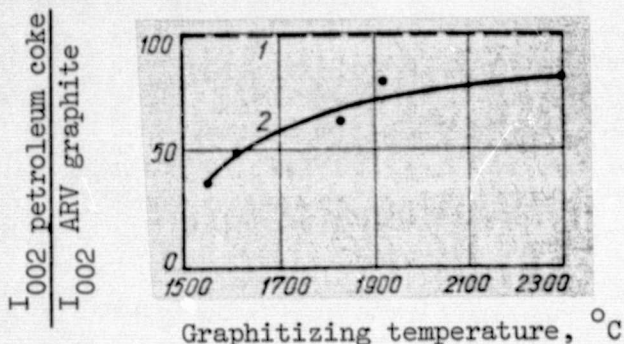


Fig. 6. Dependence of the intensity for the (002) line of petroleum coke on the graphitization temperature:

1) ARV graphite; 2) petroleum coke.

necessary to take (additionally) another series of superposition x-ray diagrams with other samples of carbonaceous materials as components. Therefore, in addition to the ARV graphite, natural graphite and petroleum coke, which had been roasted at 1550°C, were used. In addition to $B_{4.78}C$, the boron carbide $B_{6.75}C$ was used to account for the effect of the boron carbide's composition on the intensity of its lines.

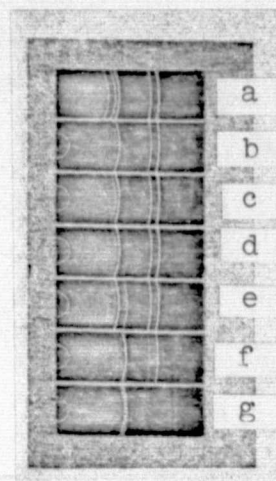


Fig. 7. Front sections of the superpositions diffraction diagrams for boron carbide $B_{4.78}C$ and ARV graphite taken with different ratios for the exposure of the components:

a) boron carbide $B_{4.78}C$;
b-f) boron carbide + graphite;
g) graphite; $t_{gr}/t_{b.c.}$: b) 0.03;
c) 0.05; d) 0.08; e) 0.13; f) 0.5.
Radiation $Co = K_{\alpha}$.

The front sections of the superposition x-ray diagrams for the boron carbide $B_{4.78}C$ and ARV graphite, taken for different exposure ratios of the components, are shown in Fig. 7. The exposure times for the boron carbide samples on the superposition x-ray diagrams were: 2.5 hrs. for the carbide $B_{4.78}C$ and 5 hrs. for the carbide $B_{6.75}C$. The exposure times for the carbon components varied from 1 to 60 min. The exposure was maintained with URS-70 clocks. The minute exposures were controlled accurately by means of a time relay PB, which was connected in the circuit of the high voltage circuit block of the URS-70 which automatically switched off the high voltage after a given exposure was finished with an accuracy of ± 0.05 min.

The operating conditions for the URS-70 device were kept constant by stabilizing the voltage on the primary coil of the high voltage transformer using the SN-1 stabilizer (127 ± 0.5 V). The radiation was $\text{Co} \rightarrow \text{K}_\alpha$.

In practice, the quantitative determination of C_{free} in boron carbide from the superposition x-ray diagram is done as follows: First, a series of x-ray superposition diagrams are taken with the D-85 camera for boron carbide and graphite with different values of the exposure ($t_{\text{gr}}/t_{\text{b.c.}}$). The ratio of the intensities of the lines for boron carbide and graphite, $I_{002 \text{ gr}}/I_{002 \text{ b.c.}}$, are determined for each photograph and a calibration curve of $I_{002 \text{ gr}}/I_{002 \text{ b.c.}} = f(t_{\text{gr}}/t_{\text{b.c.}})$ is set up.

Considering the variety of possible structural states C_{free} in boron carbide and also the wide range of possible composition and its phases (from B_4C to $\text{B}_{6.75}\text{C}$), it is necessary also to set up calibration curves for a number of combinations of boron carbides of various composition with different carbonaceous materials. Then the sample is photographed in the D-85 or any other Debye camera. Then a determination is made, on the basis of the fine structure of the (002) line for the graphite lattice (profile, width, intensity distribution), as to which free carbon the sample is closest in its structural state. The composition of the boron carbide [3] is determined from the lattice parameters (the angle θ_{002}). The blackening of the (002) line of graphite and the (110) line of boron carbide is determined as the area of the peaks on the curve for the angular distribution of the blackening. The ratio of the blackening S_{002}/S_{110} is determined, which is equal to the ratio of the intensities $I_{002 \text{ gr}}/I_{110 \text{ b.c.}}$ if we are working in the range of blackening ≤ 1 .

The ratio of the exposures $t_{\text{gr}}/t_{\text{b.c.}}$, which correspond to the given value of I_{002}/I_{110} , is found on the boundary of the curve which is set up from the superposition x-ray diagrams for boron carbide and carbon, which are identical to the sample with respect to the structural state (Fig. 8). C_{free} (Fig. 9) is read from the curve $C_f = f(t_{\text{gr}}/t_{\text{b.c.}})$ which has been set up for a boron carbide with the same composi-

tion as the sample, from the values of $t_{gr}/t_{b.c.}$.

The standard curves in Fig. 9 are set up from the system of equations [4]:

$$\frac{C_{gr} (\mu/\rho)_{b.e.} t_{gr}}{C_{b.c.} (\mu/\rho)_{gr} t_{b.e.}}$$

$$C_{gr} + C_{b.e.} = 100\%$$

where C is the concentrations of graphite and boron carbide by weight, /16
t is the exposure time for graphite and boron carbide on the superimposed photographs, μ/ρ are the mass absorption coefficients for graphite and boron carbide. In the Co-K radiation, the values of the mass absorption coefficients for the corresponding components are [1]:

Phase	Graphite	B ₄ C	B _{4.78} C	B _{6.75} C
μ/ρ	8.5	5.5	5.4	5.2

If the composition of the boron carbide differs from B₄C, B_{4.78}C, or B_{6.75}C, for which the standard curves have been set up, the C_{free} concentration is found by extrapolation. In the case in which a large number of photographs make up the series of superposition x-ray diagrams which differ by small stages of exposure, a visual selection can be made, without measuring the blackening, of the superposition x-ray diagram on which the ratio of the intensities of the analyzed lines is approximately the same as that on the x-ray diagram being studied. In this case it is recommended that the intensity of the (002) line of graphite always be evaluated with all six primary lines for boron carbide for greater accuracy.

The method was developed for the analysis of samples containing /17
up to 10% free carbon. The quantitative analysis of samples with larger C_{free} concentrations can be carried out in an analogous way; however, the (002) line of graphite should be compared with one of the more intense lines for boron carbide (102), (014) or (201) and not with the (110) line.

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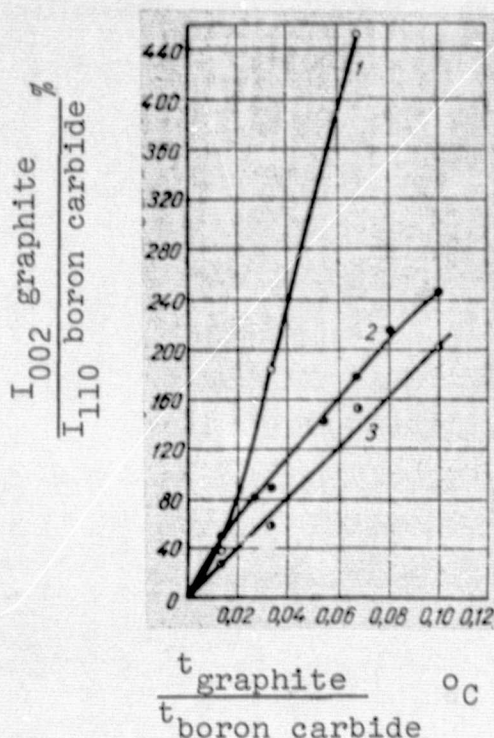


Fig. 8. Calibration curves set up from a series of superposition x-ray diagrams for different boron carbides and carbon materials:

- 1) $B_{6.75}C$ + ARV graphite;
- 2) $B_{4.78}C$ + ARV graphite;
- 3) $B_{4.78}C$ + petroleum coke roasted at 1550°C .

The following main advantages of the superposition method should be emphasized [4]:

- 1) It is not necessary to prepare standard mixtures or to add foreign phases to the sample.
- 2) The method is not dependent on chemical analysis (we need rely only on the purity and single-phase nature of the components which are used to obtain the superposition x-ray diagram).
- 3) The method can be used for very small amounts of materials.

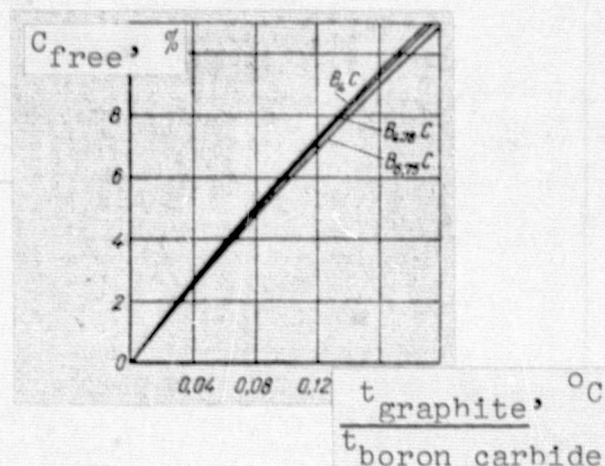


Fig. 9. Standard curves for determining the free carbon concentration in boron carbide by the superposition method.

In our studies, the superposition method seemed particularly valuable because of the very small samples of single-phase boron carbide which do not contain graphite which were available to us and which are generally rarely found.

It was found from the superposition x-ray diagrams that the lower sensitivity threshold for observing free carbon in boron carbide is about 0.15% if its structural state is analogous to Acheson graphite and about 0.3% if the carbon in the boron carbide is quite finely dispersed or has a nonequilibrium, unformed crystal lattice, i.e., if the fine structure of the (002) line for the carbon in the sample is the same as that for petroleum coke with a low level of graphitizing.

The error in parallel determinations from the superposition x-ray diagrams is 6 relative %. The reliability of the x-ray analysis is determined by the identity of the structural states for the free carbon and boron carbide in the sample and in the standard materials which are used to take the series of superposition x-ray diagrams and which are used to set up the calibrations curves.

This method can be used to analyze boron carbide samples which do not contain boron nitride in which the carbon phase is finely dispersed and is in a state of equilibrium [7] as well as in research studies: in studying the phase diagrams, to refine the results of chemical analysis, etc. Specifically, this method gave good results in analyzing boron carbon alloys produced by not pressing.

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METHOD FOR DETERMINING FREE CARBON IN MATERIALS CONTAINING REFRACTORY COMPOUNDS

L. A. Mashkovich and A. F. Kuteynikov*

Various types of carbon differ from one another by certain properties, including their reactions with chemical reagents. So-called amorphous graphite (carbon black, highly active charcoals) are readily oxidized by a 30% solution of hydrogen peroxide [10], adsorbs certain dyes (bromthymol blue, etc.) [9], whereas graphite, according to our data, remains unchanged in reactions with these reagents. Two means were studied for separating free carbon from refractory compounds in order to make a systematic study of the chemical properties of carbonaceous materials. These were the removal of the free carbon by igniting in a muffle furnace at 850°C and "wet" oxidation.

The first method was only possible for the SiC-graphite system. In the presence of other polyfluoroethylene carbides, even in the presence of boron dissolved in the silicon carbide, this method is not suitable. The oxidation of the carbides takes place along with the burning off of the free carbon and the first process predominates over the second [6] and the polyfluorethylene is totally burned up before the carbon at 600-700°C.

Various mixtures were tested in order to select the conditions for the total oxidation of the given types of carbon: 10 ml H_2SO_4 + 10 ml HNO_3 + 5 ml $HClO_4$ + 20 ml $K_2Cr_2O_7$; H_2SO_4 + $K_2Cr_2O_7$ + $HClO_4$ (with different ratios of the components), H_2SO_4 + $HClO_4$, $HClO_4$ + $K_2Cr_2O_7$, H_2SO_4 + $K_2Cr_2O_7$, HNO_3 + H_2SO_4 , H_3PO_4 + H_2SO_4 + $HClO_4$ [1,3,7,8,11].

The oxidizing action of the mixtures was checked with various types of graphite (PROG - 2400, pg-50, AG-1500, etc.), carbon blacks (gas channel, thermal, PG-33), and cokes (KNPS, cracking, furnace, aryl tars, etc.). The experiments showed that all the types of carbon

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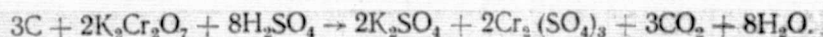
which were studied are completely oxidized only by mixtures Nos. 5 and 2 (for a 2:2:1 ratio of the components). It was found that the presence of perchloric acid (mixture No. 2) worsens the oxidizing ability of the mixture, thereby increasing the time of oxidation. From then on all of the work was done with mixture No. 5, which consists of concentrated sulfuric acid and a 5% aqueous solution of potassium dichromate in a 1:1 ratio.

TABLE 1

THE EFFECT OF THE BOILING TIME AND SULFURIC ACID CONCENTRATION ON THE REDUCTION OF CHROMIUM FOR BOILING OF THE CHROMIC MIXTURE (initial volume of 60 ml) WITHOUT REFLUXING.

Volume of chromic mixture after boiling, ml	Ratio of the components in the mixture: 5% solution of potassium dichromate + 10% sulfuric acid	Boiling time, min.	Color of the solution	Amount of reduced chromium, %
60	1:1	0	Orange	0.0
51	1:1	60	Orange-red	2.5
40	1:1	120	Dark red	10.0
29	1:1	180	Reddish green	30.0
30	1:4	180	Orange	0.8
31	1:2	180	Orange-red	3.0
28	1:1	180	Orange-red	20.0
30	2:1	180	Reddish green	80.0
30	4:1	180	Green	100.0
			Dark green	

The mechanism for the oxidation of carbon by the $H_2SO_4 + K_2Cr_2O_7$ mixture is given by the equation



In this reaction, clear-cut stoichiometry may be expected under certain conditions which can be used to determine the carbon by determining one of the forms of the chromium. In many cases this approach is promising since it allows us to determine the carbon over a wide range of concentrations. It does not require special apparatuses and it makes it possible to determine the carbon and to isolate the insoluble carbide phase or other inert substance quantitatively at the same time.

The method which we developed for determining carbon [4] is based on this principle. It was found that in oxidizing spectroscopically pure graphite with a chromic mixture having different volumetric ratios of the sulfuric acid and the potassium dichromate solutions, the time required for the complete oxidation of the graphite decreases with an increase in the sulfuric acid concentration (Fig. 1). It was shown that in a blank experiment (a mixture of sulfuric acid and a solution of potassium dichromate without the graphite) oxidation-reduction processes take place; the solution's color changes from orange to dark red and then to green, which indicates that some amount of the chromium is reduced. The amount of chromium which is reduced depends on the conditions for the blank experiment as well as on the boiling time and the sulfuric acid concentration (Table 1). The amount of reduced chromium is greater for boiling in an open flask than for boiling the same solutions with refluxing. The effect of the boiling time and of the concentration of the sulfuric acid (sp. g. 1.84) on the reduction of chromium in the blank run are shown in Fig. 2.

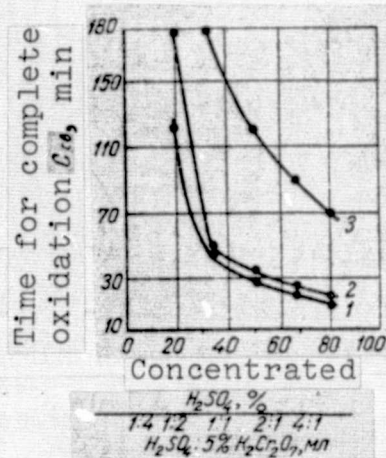


Fig. 1. Dependence of the time for complete oxidation of the free carbon on the sulfuric acid concentration in the chromic mixture:

1) 0.01 g; 2) 0.05 g; 3) 1.0 g.

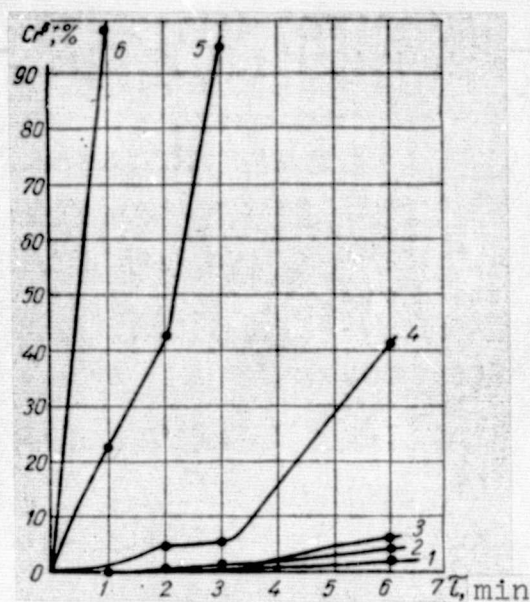


Fig. 2. Effect of the boiling time and the composition of the chromic mixture on the reduction of chromium in a blank experiment:

1 — 1H₂SO₄: 4K₂Cr₂O₇ (10%); 2 — 1H₂SO₄: 2K₂Cr₂O₇ (10%); 3 — 1H₂SO₄: 1K₂Cr₂O₇ (5%); 4 — 1H₂SO₄: K₂Cr₂O₇ (10%); 5 — 2H₂SO₄: K₂Cr₂O₇ (10%); 6 — 4H₂SO₄: 1K₂Cr₂O₇ (10%).

It is not recommended that a 10% solution of potassium dichromate be used in preparing the oxidizing mixtures, since a large amount of the potassium dichromate precipitates out of such solutions upon standing. In mixtures of sulfuric acid (sp. g. 1.84) with a 5% solution of potassium dichromate 0.002-0.003 g of the chromium are oxidized for a 1:1 ratio of the components and for boiling for 2-3 hrs. This equals 0.02-0.3% of the chromium used. /21

For prolonged boiling of the solutions (5-11 hrs.) the amount of chromium reduced increases to 0.04-0.07 g, which is equal to 5-9% of the amount used.

TABLE 2
RESULTS OF DETERMINING FREE CARBON BY OXIDATION WITH
DICHROMATE

Amount of spectroscopically pure graphite, mg.	Amount of hexavalent chromium used in the oxidation of the graphite, mg			Carbon obtained, mg (arithmetic average from 10 determinations)	Absolute error, mg	Relative error, %
	Calculated from the reaction	Determined experimentally (arithmetic average from 10 determinations)	Deviation from calculated value			
5.0	28.9	30.5	+1.6	5.3	+0.3	5.6
10.0	57.8	58.7	+0.9	10.2	+0.2	2.0
20.0	115.7	118.1	+2.4	20.4	+0.4	2.0
40.0	231.1	231.6	+0.5	40.1	+0.1	0.25
60.0	346.7	344.3	-2.4	60.0	0	0
80.0	462.2	449.7	-12.5	77.8	-2.2	2.75
100.0	577.8	579.0	+1.2	100.2	+0.2	0.20

A mixture containing 20 volume % sulfuric acid oxidizes graphite too slowly and is not very suitable. The most reasonable mixture is one with a sulfuric acid to potassium dichromate ratio of 1:1 or 1:12 (potassium dichromate was used in the form of a 5% aqueous solution). Such mixtures oxidize 1 gram of free carbon in 2-3 hrs. In this period of time only 0.3% of the chromium is reduced in the blank experiment. Taking the results of the blank into account, the error due to this can be excluded or lowered to a minimum.

From here on the free carbon was oxidized with a mixture of

sulfuric acid and 5% solution of potassium dichromate (1:1) in a flask with refluxing (a blank was run at the same time). The series of experiments on the oxidation of spectroscopically pure graphite (Table 2) showed a direct proportionality between the carbon which is present and the amount of chromium which is used to oxidize it. Consequently, the oxidation-reduction reaction between the carbon and the chromium under the given conditions takes place stoichiometrically, and the amount of /22 chromium which is used in the oxidation can be used to calculate the carbon concentration.

The statistical treatment of the results gave the relative error for the method which was 4-7% in determining small amounts of carbon (0.04-0.005 g) and \leq 3.5% in determining amounts up to 0.1 g.

Method of Analysis

A sample of the material weighing 0.2 g (containing 50% free carbon) was pulverized to 200 mesh and treated with 50 ml. of a 5% solution of potassium dichromate, measured accurately with a burette, and 50 ml. of concentrated sulfuric acid with boiling in a 200-300 ml tapered flask fitted with a ground glass reflux condenser for 2-3 hrs. A blank was run at the same time. After dissolution, the flask's contents with the residue are transferred to a 250 ml volumetric flask.

The residue, which is made up of refractory compounds, is removed from the solution by centrifuging, washed with water until a neutral reaction is reached using methyl red. It is then dried in a dessicator at 100°C and weighed.

A 0.05 N solution of Mohr's salt is added to an aliquot portion (25/250 for the sample and 5/250 for the blank) from a burette and the excess is titrated with a 0.05 N solution of potassium permanganate [2]. The amount of carbon is calculated by using the formula

$$x = \frac{A \cdot 100}{5.78 \cdot a},$$

where x is the carbon concentration, %, a is the sample weight in g,

TABLE 3
COMPARATIVE DATA ON THE OXIDIZABILITY OF SOME CARBONACEOUS
MATERIALS

Sample Material	Time required for complete oxidation, min.
PG-33	20-25
Carbon black	20-25
thermal	
gas channel	
KNPS, not roasted	10-20
Coke	10-20
cracking furnace	
KNPS - graphitized	160-180
Graphite	160-180
PROG-2400	
ZOPG	
PG-50	
ARV	
Natural	
AG-1500	

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and 5.78 is the amount of chromium used to oxidize 1 g of carbon, and /23
A is the amount of chromium used to oxidize the free carbon in the
sample. $A = B_1 - B$. The value of B_1 is found in titrating the blank
and B is found from titrating the sample from the formula

$$B = [C \cdot v_1 - V] \cdot T \frac{\text{KMnO}_4}{\text{Cr}} \cdot b,$$

where $C = V'/V''$ is the ratio between the solutions of Mohr's salt
(v'') and the potassium permanganate (v'), v_1 is the amount of Mohr's
salt (in ml) added to the aliquot, v is the amount of potassium per-
manganate (in ml) used in the back titration, b is the dilution.

The data on the oxidation of different types of carbonaceous
materials with a mixture of sulfuric acid and potassium dichromate
are given in Table 3. Since it requires 3 hrs. for the complete oxi-
dation of structurally-free graphite -- the most chemically stable of
the carbonaceous materials -- the oxidizability of some refractory
compounds was studied under identical conditions (Table 4).

TABLE 4

Sample Material*	Amount of oxidized carbon, %												
	5 min	10 min	15 min	20 min	30 min	45 min	1 hr.	1 hr 15 min	1 hr 30 min	1 hr 45 min	2 hr 15 min	2 hr 30 min	2 hr 30 min
Graphite PROG-2400 (0.02 g)	—	—	—	18,0	—	18,78	19,51	20,62	20,62	17,32	20,46	20,52	21,35
B ₄ C	3,02	4,2	4,24	3,8	9,2	7,73	8,09	8,84	—	8,73	9,71	—	10,9
Mixture of B ₄ C (0.08 g) + + C (0.02 g)	14,79	—	17,37	19,57	27,25	21,2	24,67	26,52	25,79	25,91	28,00	28,58	28,8

*Sample weight 0.1 g.

As our experiments showed, the oxides (Al_2O_3 , Fe_2O_3 , and SiO_2) do not dissolve in the chromic mixture, but B_2O_3 and P_2O_5 dissolve completely since the elements in these oxides have a higher valence, the chromium is not used in their oxidation. Silicon, silicon carbide, tantalum carbide and polyfluorethylene do not dissolve and are not oxidized by the mixture; consequently, their presence does not interfere with the determination of the free carbon by this method. Boron carbide behaves differently in the chromic mixture depending on the method for its preparation and its dispersion. Boron carbide prepared from PROG-2400 graphite pulverized to 150 mesh was quite stable to oxidation. The results of determining the amount of free carbon by the graphic, gravimetric [7], and the present method are quite similar.

Since the rate of oxidation of the carbon is much greater than the rate of oxidation of the boron carbide, the given method for phase separation and determination of free carbon is applicable, particularly for large (over 10%) carbon concentrations.

The given method was checked on synthetic mixtures and on commercial samples. The results are given in Tables 5 and 6.

TABLE 5
RESULTS OF DETERMINING FREE CARBON IN VARIOUS MATERIALS

Material, g		Free carbon found	
Silicon carbide (boron carbide)	Graphite	g	%
—	0,0500	0,0498	99,60
0,5000	—	0,0005	0,10
0,5000	0,0500	0,0502	9,13
1,0000	0,0100	0,0107	1,06
0,1000	—	0,0110	11,0
0,1000	—	0,0106	10,60
0,1000	—	0,0111	11,01
0,5000	—	0,0560	11,20
0,1000	0,0200	0,0305	25,41
0,1000	0,0100	0,0207	18,82
0,1000	0,0300	0,0398	36,15
Polyfluoroethylene			
0,9000	—	0	0
0,9000	0,1000	0,0986	9,86
0,9200	0,0800	0,0794	7,94

CONCLUSIONS

1. The optimum conditions were found for determining carbon by means of the oxidation-reduction reaction with a mixture of potassium dichromate and sulfuric acid. /25
2. A method was developed for determining carbon directly from the oxidation-reduction reaction between the carbon and the chromium by determining the amount of reduced chromium.
3. The method is applicable for separating and determining the free carbon in materials which contain refractory compounds. /26

TABLE 6
COMPARATIVE DATA ON DETERMINING THE FREE CARBON
BY DIFFERENT METHODS

Sample Material	Free carbon concentra- tion from specifica- tions or by calculation	Free Carbon Found, %		
		This method	Heating in muffle fur- nace at 850°C	Gas- volume method
Silicon carbide	0.12	0.10	—	0.12
Artificial mixture				
silicon carbide-	50	50.10	50.0	—
graphite	10	10.13	9.85	9.96
Samples of the				
SiC-graphite				
system				
No. 1	—	1.34	1.20	1.27
No. 2	—	61.47	61.10	—
No. 3	—	61.08	60.50	—
No. 4	—	67.02	67.7	—
No. 5	—	81.44	82.1	—
Type II boron carbide	Do 18	10.60	—	10.07
Sample from the boron-silicon-				
carbon system	—	63.75	44.82 ¹	62.62
Polyfluoroethylene ²	0	0	—	—
Artificial mixture	10	9.86	—	—
polyfluoroethylene-graphite	8	7.94	—	—
Samples of the polyfluoroethylene-				
graphite system				
No. 1	50	50.30	—	—
No. 2	50	52.10	—	—
No. 3	65	66.80	—	—

¹Using method based on heating the free carbon in a muffle furnace at 850°C, to analyze samples containing boron. Samples containing boron cannot be analyzed by the method based on roasting the free carbon in a muffle furnace at 850°C since the results for free carbon are great-
lowered because of the oxidation of the boron.

²The samples which contain polyfluoroethylene cannot be determined by the heating and gas volume methods.

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THE STABILITY OF COMPOUNDS OF THE BORON-CARBON SYSTEM IN OXYGEN AT HIGH TEMPERATURES

L. Ye. Pechentkovskaya and T. N. Nazarchuk*

Alloys based on boron are widely used because of their many useful properties. In almost all cases they are used because of their main property -- their refractory nature.

The processes for the high temperature oxidation of such compounds as the carbides and nitrides are complicated by the fact that gaseous products are formed along with the solid oxidation products. The object of this work was to study the oxidation of alloys of boron with carbon at various temperatures.

According to Moissan's data [7], oxygen does not oxidize boron carbide at temperatures up to 500°C and at 1000°C the latter burns in a stream of oxygen forming CO_2 and B_2O_3 .

Ridgway [8] studied the oxidizability of boron carbide with time at different temperatures. G. A. Meyerson and G. V. Samsonov [2] studied the oxidation of boron carbide at various temperatures: 820, 1040 and 1080°C. On the basis of the results on the rate of oxidation of boron carbide, an attempt was made to develop a method for determining the free carbon in it. 127

A study of the oxidation of boron carbide at various temperatures in the 600-1300°C range [3] showed that it begins at 700°C. Complete oxidation is observed at 1200-1300°C, in which case the stability of the boron carbide to oxidation depends on the carbon that is present in it.

The oxidizability was studied for alloys of the boron-carbon system to determine the effect of the chemical composition on their

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stability in oxygen. For this study, alloys were used containing various concentrations of carbon and boron. The samples were analyzed for the boric anhydride, free boron and carbon concentrations (Table 1). The boric anhydride was not observed in any of the samples.

The oxidation was carried out in a tubular Silit furnace for a constant flow of oxygen at 500 - 1300°C at flow rates of 200 ml/min. The degree of oxidation was judged from the amount of carbon and boron oxides in equal periods of time.

TABLE 1
CHEMICAL COMPOSITION OF THE
SAMPLE ALLOYS, %

Alloy No.	C _{free}	B _{total}	B _{free}
1	13.9	82.7	0.26
2	15.5	82.4	Not found
3	17.9	80.3	" "
4	20.2	79.1	" "
5	22.3	76.8	" "
6	24.8	73.2	0.05
7	27.9	71.3	0.10
8	30.1	68.3	0.10

As we can see from Figs. 1 and 2, the oxidation of boron-carbon alloys begins at 500°C. At this temperature the oxidation can only be observed from the formation of B₂O₃. The carbon in the alloy (even for concentrations of 30.1%) is not oxidized at all even at this temperature. A slight oxidation is observed for the carbon at 600°C. Actually, the oxidation of the boron-carbon alloys begins at a temperature of 700°C. At 700-1200°C, the oxidation of the boron carbide, for all boron to carbon ratios, takes place in some fixed period of time and then it ceases. /28

A sharp increase in the oxidation is observed at 1200-1300°C, i.e., at a temperature for which the volatility of B₂O₃ oxide film which is formed up to 1200°C protects the boron carbide to some extent from further oxidation.

Although the oxidation curves for all of the alloys of the boron-carbon system have a unique character (see Figs. 1 and 2), it is not difficult to notice the following regularity: As the carbon concentration in the alloy increases, its stability to oxidation decreases. In our case, the most stable alloy with respect to oxidation is alloy 1

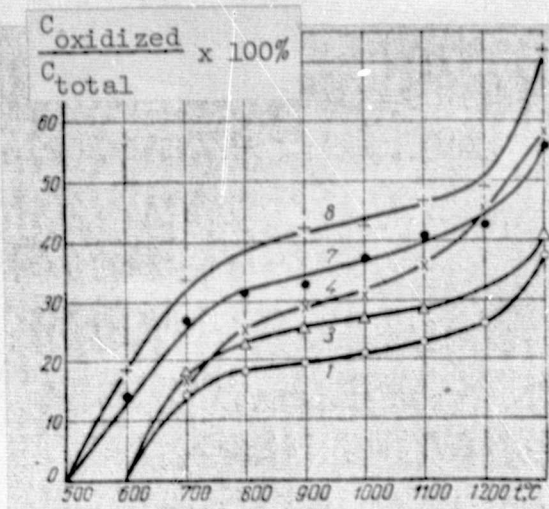


Fig. 1. Oxidation curves for boron-carbon alloys (with respect to carbon). Here and in the following figures, the number on the curve corresponds to the alloy's number in Table 1.

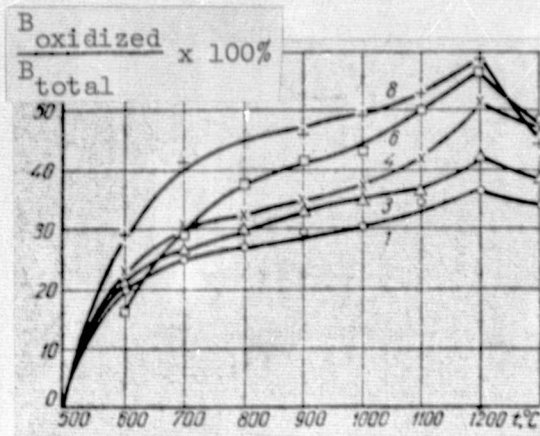


Fig. 2. Curves for the oxidation of boron-carbon alloys (with respect to boron).

(13.9% C) and the least stable is alloy 8 (30.1% C).

The oxidation process for the alloys of the boron-carbon system /29 appears to be the following: At low temperature (400-600°C), the boron is oxidized, apparently those atoms which occupy the least stable positions in the lattice. At 600°C the carbon atoms also undergo oxidation. The percentage of oxidized boron at this temperature greatly exceeds the percentage of oxidized carbon (Table 2). At 700°C the oxidation of carbon takes place vigorously. The ratio of the oxidized boron to the oxidized carbon decreases and at 800°C it becomes stable, becoming almost constant (Fig. 3).

We can see from Fig. 3 that the curves 1, 2 and 3 for the alloys with a more defective structure have a clearly expressed inflection. The amount of oxidized boron greatly exceeds the amount of oxidized carbon. The alloys appear to try to give up the "excess" boron, the C-B-C line of the crystal lattice converts to the C-C-C line for boron carbide ($B_{12}C_3 (=B_4C)$). For samples with a less defective structure, such an abrupt formation of boron is not observed.

TABLE 2
OXIDATION OF BORON-CARBON AT VARIOUS TEMPERATURES

Alloy No.	Concentration in alloy, %	Relative Percent Oxidation											
		500° C			600° C			700° C			800° C		
		B	C	B	B	C	B	B	C	B	B	C	B
1	13.9	1.4	0	20.0	1.3	0	25.0	14.2	26.1	18.3	28.7	19.6	30.2
2	15.5	4.5	0	21.3	0.5	0	26.4	14.6	27.7	15.2	28.6	19.0	31.0
3	17.9	0.8	0	21.5	0.6	0	28.1	18.5	29.1	22.7	34.3	26.0	35.6
4	20.2	2.4	0	22.0	11.8	0	30.2	16.2	32.3	25.6	35.0	29.0	36.8
5	22.3	1.5	0	13.3	0.8	0	29.6	17.3	33.6	19.6	38.8	27.3	39.4
6	24.8	6.0	0	16.3	0.3	0	30.2	15.3	37.4	31.7	40.7	33.6	43.6
7	27.9	1.5	0	27.8	13.9	0	33.6	26.9	38.9	31.7	40.8	32.2	41.2
8	30.1	0.4	0	28.6	18.9	0	42.4	33.2	44.0	37.6	46.6	42.0	49.0
1000° C													
		B	C	B	B	C	B	B	C	B	B	C	B
		21.5	21.5	30.2	21.5	21.5	34.6	23.1	34.6	36.0	26.4	26.4	34.6
		20.8	20.8	31.0	20.8	20.8	32.6	22.0	32.6	40.1	31.3	31.3	36.2
		27.5	27.5	35.6	27.5	27.5	36.6	29.0	36.6	42.6	30.5	30.5	38.6
		31.1	31.1	36.8	31.1	31.1	42.4	36.9	42.4	51.5	45.7	45.7	47.7
		29.1	29.1	39.4	29.1	29.1	43.4	32.9	43.4	55.2	44.5	44.5	56.1
		36.3	36.3	43.6	36.3	36.3	50.6	44.4	50.6	57.3	47.7	47.7	47.3
		37.9	37.9	49.0	37.9	37.9	48.9	42.3	48.9	47.0	42.2	42.2	46.8
		42.7	42.7		42.7		52.8	46.7	52.8	53.0	48.8	48.8	27.3
1200° C													
		B	C	B	B	C	B	B	C	B	B	C	B
		34.7	34.7	34.6	34.6	34.6	34.6	23.1	34.6	36.0	26.4	26.4	34.6
		41.5	41.5	36.2	36.2	36.2	32.6	22.0	32.6	40.1	31.3	31.3	36.2
		44.0	44.0	38.6	38.6	38.6	36.6	29.0	36.6	42.6	30.5	30.5	38.6
		58.4	58.4	47.7	47.7	47.7	42.4	36.9	42.4	51.5	45.7	45.7	47.7
		62.0	62.0	56.1	56.1	56.1	43.4	32.9	43.4	55.2	44.5	44.5	56.1
		55.8	55.8	47.3	47.3	47.3	50.6	44.4	50.6	57.3	47.7	47.7	47.3
		56.3	56.3	46.8	46.8	46.8	48.9	42.3	48.9	47.0	42.2	42.2	46.8
		74.1	74.1	27.3	27.3	27.3	52.8	46.7	52.8	53.0	48.8	48.8	27.3

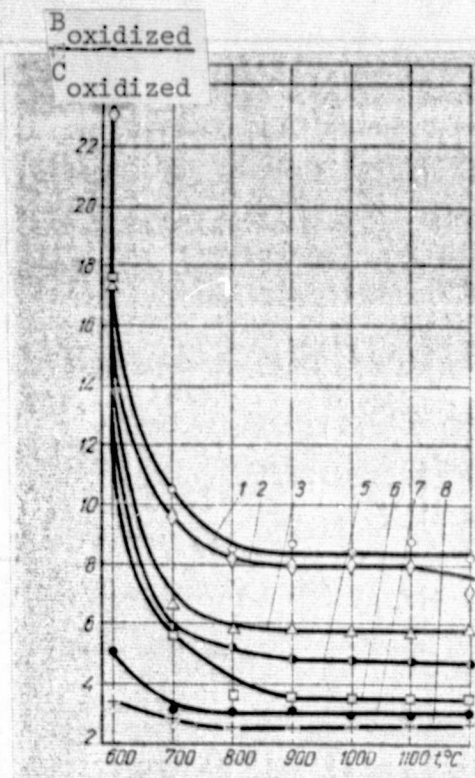


Fig. 3. The ratio of oxidized boron to oxidized carbon at different temperatures.

As we can see from this figure, the ratio $\frac{B_{\text{oxidized}}}{C_{\text{oxidized}}}$ becomes constant at 800°C. In this connection, the question arises of whether all the alloys of the boron-carbon system are oxidized to some given composition which is the most stable composition for this system, or if there is a most characteristic structure for each alloy with a given [B] : [C] ratio.

In order to answer this question, boron-carbon alloys were oxidized with oxygen at 600, 800 and 1200°C. Up to the time for which the oxidation had not as yet ceased ($\frac{\Delta C}{\Delta t} = 0$). The samples which remained after oxidation were washed

to remove the boric anhydride, dried, and the boron and carbon concentration was determined in them. It was assumed that for this treatment of the alloys, free boron and carbon, which were the main hindrances in determining the composition for compounds of the boron-carbon system by chemical means, were oxidized first.

As the data in Table 3 shows, alloys 1 and 2 (containing 13.9 and 15.5% carbon in the initial samples) strive to form the compound $B_{11}C_2$. For the oxidation of the alloy containing 17.9% carbon in the initial sample, a compound is formed with a composition corresponding to the formula $B_{4.6}C$.

For the oxidation of alloys containing from 22.3 to 27.9% carbon, the oxidation product for all the alloys and at all temperatures (after removal of the B_2O_3) is a compound whose composition corresponds to the formula B_3C . The alloy containing 30.1% carbon forms a compound with the formula $B_{12}C_5$ ($B_{2.4}C$).

These studies allow us to prove beyond doubt that the formation of four individual substances is possible in the boron carbon system. Their composition corresponds to the formulas $B_{11}C_2$, $B_{4.6}C$, B_3C and $B_{12}C_5$.

These results agree with some literature data. Glasser and Moskowitz [6] studied boron carbide because of its similarity with the structure of boron in solutions of various amounts of carbon in a slightly distorted boron lattice in whose voids there is sufficient space for the placement, at the maximum, of two additional atoms. Such an explanation was given for the compound $B_{12}C_5$ which they also prepared.

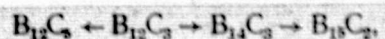
Clark and Hoard [5] suggested that there is sufficient space in the elementary cell of boron carbide so that it could be filled with two additional boron atoms. The filling of such "holes" with boron atoms, in their opinion, leads to the formation of boron carbide with the composition $B_{14}C_3$ which corresponds to $B_{4.67}C$.

TABLE 3

CHANGE IN THE COMPOSITION OF THE ALLOYS IN THE BORON-CARBON
SYSTEM DURING OXIDATION AT DIFFERENT TEMPERATURES

Composition of the initial sample (before oxidation)				Composition of the compound after removing the oxidation products			
Alloy No.			Calculated composition				
	B, %	C, %		600° C	800° C	1000° C	1200° C
1	82.7	13.9	$B_{13}C_2$	$B_{5.6}C$	$B_{5.4}C$	$B_{5.3}C$	—
2	82.4	15.5	B_6C	B_6C	$B_{3.5}C$	$B_{3.5}C$	$B_{5.5}C$
3	80.3	17.9	B_5C	—	$B_{4.6}C$	$B_{4.6}C$	$B_{4.6}C$
4	76.8	22.3	$B_{3.6}C$	$B_{3.9}C$	$B_{3.6}C$	B_3C	$B_{3.1}C$
5	73.2	24.8	$B_{3.2}C$	$B_{3.2}C$	$B_{3.2}C$	$B_{3.2}C$	—
6	71.3	27.9	B_3C	B_3C	B_3C	B_3C	B_3C
7	68.3	30.1	$B_{2.45}C$	$B_{2.5}C$	$B_{2.5}C$	$B_{2.4}C$	$B_{2.4}C$

V. I. Kudryavtsev and G. V. Sofronov [1] think that it is possible to prepare a continuous series of solid solutions of boron carbide according to the scheme



where $B_{12}C_3$ has the boron carbide lattice in which the voids (holes) are vacant, i.e., they are not occupied by either boron or carbon atoms. $B_{12}C_5$ and $B_{14}C_3$ have lattices in whose cavities two additional atoms and two additional boron atoms are freely situated, respectively.

Thus, the existence of compounds whose compositions correspond to the formulas $B_{12}C_{4.5}$ and $B_{4.6}C$ was confirmed by these authors. The compound B_3C ($B_{12}C$), can be represented as a solid intrusion solution based on the cell $B_{12}C_3$, in which an additional carbon atom is placed. Proceeding from these concepts, the compound $B_{11}C_2$ ($B_{5.5}C$) can be thought of as a compound with an already distorted boron carbide lattice. Let us recall that the presence of such a compound with the arbitrary stoichiometric formula $B_{5.66}C$ was indicated by Allen [4].

1. It was shown, as the result of studying the oxidation of alloys in the boron-carbon system, that as the carbon concentration in the alloy increases, the alloy's resistance to oxidation decreases.
2. The oxidation of the alloys begins at 500°C. At 800-1200°C, the ratio $\frac{B_{\text{oxidized}}}{C_{\text{oxidized}}} = \text{const.}$ For samples with a defective structure, a marked oxidation of the boron is observed.
3. Each alloy of the boron-carbon system is oxidized to a composition which is characterized by a given stoichiometric formula. In this way, the presence of four compounds was established for the boron-carbon system. These have the arbitrary stoichiometric formula: $B_{11}C_2$, $B_{4.6}C$, B_3C and $B_{12}C$ ($B_{2.4}C$).

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SOME OF THE CHEMICAL PROPERTIES OF BORON CARBONITRIDE

L. E. Pechentkovskaya and T. N. Nazarchuk*

Refractory compounds have recently occupied a strong position in science and technology. One of these is boron carbonitride, which is a refractory substance stable to the action of various reagents. It is relatively new and has not been studied to any great extent.

In this work, some of the chemical properties of boron carbonitride were studied, particularly its reaction with calcium oxide and barium carbonate in a stream of oxygen and carbon dioxide as well as its reaction with carbon dioxide.

THE REACTION OF BORON CARBONITRIDE WITH
CALCIUM OXIDE AND BARIUM CARBONATE IN A
STREAM OF OXYGEN

Boron carbonitrides with the following compositions were used:

BNC № 1 — 63,5% — B;	12,4% — C;	23,7% — N
BNC № 2 — 54,4% — B;	5,1% — C;	39,1% — N
BNC № 3 — 48,3% — B;	5,8% — C;	39,0% — N

The finely ground powder of the boron carbonitride was mixed in a porcelain combustion boat with calcium oxide which had been dried at 120°C in a 1 : 4 ratio. The boat was set in a tubular furnace to which an oxygen source was connected, and the cold furnace was blown out with oxygen for one hour. The furnace was switched on and the temperature was raised to 900°C while oxygen was passed through for 1.5 hours. The gaseous reaction products were collected.

At the end of the experiment, the gas mixture was analyzed on the VTI-2 apparatus. The sintered mass was dissolved in water by

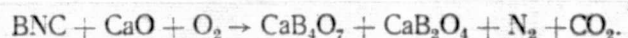
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boiling. The insoluble residue was filtered off. The boron concentration in the water extract was determined by titration with alkali in the presence of mannite using phenolphthalein and calcium oxalate method. The oxygen was determined by calculation. The analysis showed that calcium polyborate with the composition CaB_2O_4 goes into the aqueous extraction.

Experiments analogous to the foregoing were carried out to determine the composition of the insoluble compounds; however, the ratio of the boron carbonitride to the calcium oxide in the roasting was 4 : 1. The resulting cake was boiled for about 1 hour in water and the insoluble residue was filtered off and treated with 5% hydrochloric acid with boiling and the calcium and boron were determined (Table 1).

Consequently, judging from the analysis, a calcium borate having the composition CaB_4O_7 , which is insoluble in water, is also formed. The results of the gas analysis showed that the gaseous reaction products are carbon dioxide and nitrogen.

Summing up the foregoing, the reaction between the boron carbonitride and the calcium oxide in the stream of oxygen can be represented in the following way:



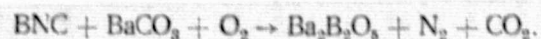
Analogous experiments were made to explain the reactions for the roasting of boron carbonitride with barium carbonate. One gram of the boron carbonitride and 1 g of barium carbonate were mixed in a porcelain combustion boat and roasted for 3 hours in a flow of oxygen at 800-850°C. The sintered mass was dissolved in water with boiling. The boron and barium concentrations were determined in the water extract by precipitation in the form of the sulfate). The results of these studies are given in Table 2.

Thus, the polyborate with the composition $\text{Ba}_2\text{B}_2\text{O}_5$ was formed from the roasting of boron carbonitride with barium carbonate in a stream of oxygen.

TABLE 1

No. BNC	Found B^{3+} , g-ions	Ca ²⁺ Found g-ions	O^{2-} Concentration (calculated) g-ions	Calculated formula
1	$2.78 \cdot 10^{-3}$	$0.7 \cdot 10^{-3}$	$4.9 \cdot 10^{-3}$	CaB_4O_7
2	$1.41 \cdot 10^{-3}$	$0.35 \cdot 10^{-3}$	$2.3 \cdot 10^{-3}$	CaB_4O_7
3	$2.76 \cdot 10^{-3}$	$0.7 \cdot 10^{-3}$	$4.9 \cdot 10^{-3}$	CaB_4O_7

In addition to oxygen, nitrogen and carbon dioxide were found in the gas phase. Therefore, the reaction can be expressed as:



It should be noted that boron carbonitride does not sinter completely with the barium carbonate. This, apparently, is due to the fact that at the given temperature a fused bead is formed from the reaction of the barium carbonate and the boron carbonitride. The availability of the oxygen ceases and the reaction stops. Therefore, it is recommended that a mixture of barium carbonate and calcium oxide be used in the sintering of the boron carbonitride in which the calcium oxide acts as a loosening agent.

TABLE 2

BNC	B^{3+} Found g-ions	Ba^{2+} Found g-ions	O^{2-} Concentration (calculated) g-ions	Calculated formula
№ 1	$3.1 \cdot 10^{-3}$	$2.7 \cdot 10^{-3}$	$7.2 \cdot 10^{-3}$	$Ba_3B_3O_5$
№ 1	$5.6 \cdot 10^{-3}$	$5.1 \cdot 10^{-3}$	$13.5 \cdot 10^{-3}$	$Ba_3B_4O_5$
№ 2	$5.8 \cdot 10^{-3}$	$5.5 \cdot 10^{-3}$	$14.2 \cdot 10^{-3}$	$Ba_3B_3O_5$
№ 2	$2.9 \cdot 10^{-3}$	$2.9 \cdot 10^{-3}$	$7.3 \cdot 10^{-3}$	$Ba_2B_2O_5$
№ 3	$1.2 \cdot 10^{-3}$	$1.1 \cdot 10^{-3}$	$2.9 \cdot 10^{-3}$	$Ba_3B_2O_5$

REACTION OF BORON CARBONITRIDE WITH CALCIUM OXIDE
IN A STREAM OF CARBON DIOXIDE

135

Finely ground powder of boron carbonitride was mixed in a porcelain combustion boat with calcium oxide, which had been dried at 120°C, in a ratio of 4 : 1. This was placed in a porcelain tube and the carbon dioxide source was switched on. The flow of carbon dioxide was continued for half an hour and then the temperature was raised to 900°C and the flow of carbon dioxide was continued for two hours. The gaseous reaction products were collected. The sintered mass which is formed was dissolved in water by boiling for one hour. The insoluble residue was treated with 5% hydrochloric acid. The barium and calcium concentrations were determined in the water and acid extract. The results are given in Table 3 for the acid extract.

TABLE 3

BNC	B ³⁺ Found g-ions	Ca ²⁺ Found g-ions	Concentration of O ²⁻ -(calculated) g-ions	Calculated formula
№ 1	2.71 · 10 ⁻³	0.7 · 10 ⁻³	4.9 · 10 ⁻³	CaB ₄ O ₇
№ 1	3.0 · 10 ⁻³	0.72 · 10 ⁻³	5.0 · 10 ⁻³	CaB ₄ O ₇
№ 2	1.42 · 10 ⁻³	0.35 · 10 ⁻³	2.5 · 10 ⁻³	CaB ₄ O ₇
№ 2	2.46 · 10 ⁻³	0.63 · 10 ⁻³	4.4 · 10 ⁻³	CaB ₄ O ₇

Thus, the product of the reaction between boron carbonitride and calcium oxide and carbon dioxide is a polyborate having the composition CaB₄O₇.

The analysis of the aqueous extract showed that the boron concentration in all cases is much higher than would be expected from the reaction (Table 4), which may be explained by the oxidation of the boron carbonitride by the carbon dioxide.

The following experiments were made to explain the nature of the reaction between boron carbonitride and carbon dioxide. Samples of boron carbonitride weighing 0.2 g were kept in a stream of carbon diox-

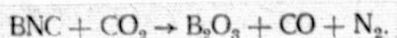
ide for 15 min. at various temperatures and then they were treated by boiling water for 1 hr., filtering the sample and determining the boric anhydride in the filtrate. As we can see from Fig. 1, the oxidation of the boron carbonitride sets in at 700°C and increases sharply with an increase in temperature.

TABLE 4

BNC	B ³⁺ Found g-ions	Ca ²⁺ Found g-ions	B : Ca Ratio
№ 1	7.3 · 10 ⁻³	1.2 · 10 ⁻³	6.0
№ 1	7.1 · 10 ⁻³	0.7 · 10 ⁻³	9.4
№ 1	4.0 · 10 ⁻³	0.8 · 10 ⁻³	5.0

/36

The analysis of the gaseous products from the reaction of boron carbonitride and carbon dioxide showed that the mixture contains nitrogen and significant amounts of carbon monoxide in addition to the carbon dioxide. Obviously, the following reaction takes place between the boron carbonitride and carbon dioxide:



In addition, the sintered mass which is found in the combustion boat is covered with a black layer of free carbon whose presence is confirmed by burning the insoluble residue in a stream of oxygen at 600°C. If the same weight of the boron carbonitride is burned without preliminary treatment with carbon dioxide, the free carbon is hardly observed at all (Table 5).

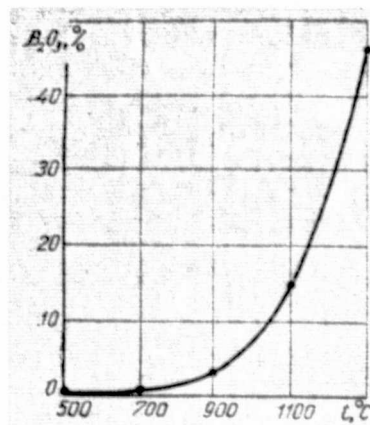


Fig. 1. Oxidation of boron carbonitride in a stream of carbon dioxide at different temperatures.

In summing up the foregoing, the reaction between the boron carbonitride, calcium oxide and carbon dioxide can be represented in the following way:

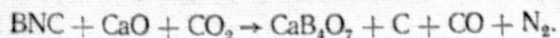


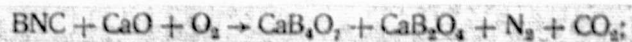
TABLE 5

BNC	Sample weight	C _{free} Con- centration, g
No. 1 (after the reaction with CO ₂)	0,2100	0,51 · 10 ⁻²
No. 2 (after the reaction with CO ₂)	0,2011	1,46 · 10 ⁻²
No. 1	0,2006	0,03 · 10 ⁻²

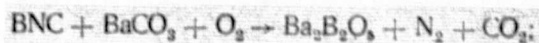
CONCLUSIONS

As a result of studying the reaction of boron carbonitride with calcium oxide and barium carbonate in a stream of oxygen and carbon dioxide at 800-900°C, it was found that:

1) boron carbonitride reacts with calcium oxide in a stream of oxygen according to the scheme:

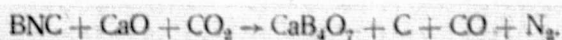


2) the reaction of boron carbonitride with barium carbonate takes place in a stream of oxygen in the following way:



3) at high temperatures, boron carbonitride is oxidized in a stream of carbon dioxide;

4) the reaction of boron carbonitride with calcium oxide in a stream of carbon dioxide is as follows:



/37

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Concentrated sulfuric acid decomposes all of the carbides at 200-300°C. The zirconium and hafnium carbides decompose at 200-230°C. The zirconium and hafnium carbides decompose at 200-230°C with the formation of amorphous carbon and methane as the main gaseous product (50-70 volume %). The titanium, vanadium, niobium and tantalum carbides decompose at 250-300°C with the formation of amorphous carbon. The gaseous products contain hydrogen, carbon monoxide and carbon dioxide. Nitric acid, being a strong oxidizing agent, decomposes titanium, niobium, zirconium, and vanadium carbides with the formation of carbon dioxide. The niobium and tantalum carbides are decomposed by nitric acid in the presence of ammonium fluoride.

The results of studying the composition of the gaseous decomposition products formed from the carbides with phosphoric and sulfuric acid confirm the data on the chemical stability and lead to the conclusion that the zirconium and hafnium carbides have a large amount of ionic Me-C bond.

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OXIDATION OF THE PHOSPHIDES OF BORON, GALLIUM,
AND INDIUM IN AIR

L. L. Vereykina*

Recently the behavior of phosphides in various gas media and their stability to the oxygen in the air has become of great interest in connection with the development of methods for producing single crystals of compounds of the $A^m B^n$ type using gas transport reactions [5] in which the starting material is often powdered phosphide.

Information on the stability of the boron, gallium and indium phosphides available in the literature is very limited. I. Yu. Andreyeva and G. V. Yefremov [1] have indicated that in the presence of small amounts of oxygen, the phosphate BPO_4 is formed in the chlorination and nitriding of boron phosphide. G. A. Goryunova [2] has published data on the initial temperature for the oxidation of the gallium and indium phosphides. It was shown that gallium phosphide starts to be oxidized at about 875° and indium phosphide at 500°C . However, no quantitative data are given on the oxidation of the phosphides either in the powdered or compact state. /38

The oxidation of boron, gallium and indium phosphides (sample weight 0.5 g) by oxygen was studied first for a preliminary evaluation of the oxidation of phosphides. The oxygen from a tank was passed through a drying system and then supplied to the reactor. As the furnace was heated, the combustion boat containing the sample was outside the heating zone and, after the required temperature was reached, it was placed inside the furnace and the time of the experiment was counted from this point. The flow rate for the oxygen was kept equal to 0.1 l./min. and it was controlled with a U-shaped liquid rheometer. Sixty milliliters of 0.2N NaOH + 1 ml 0.1 N $KMnO_4$ in two-three capillary absorption columns was used for the absorption. Such a set-up for the absorption column allowed the flow of gases from the system to be divided evenly. The solutions in the absorption columns were

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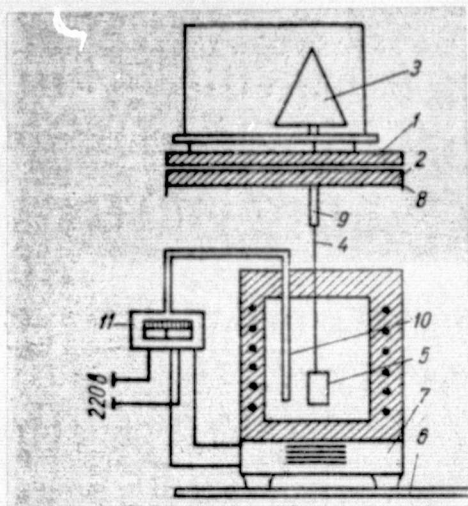


Fig. 1. Scheme of the apparatus for oxidizing the phosphides in air:

- 1) marble slab; 2) support;
- 3) thermo-balances; 4) platinum filament; 5) container with the sample; 6) slab; 7) vertical muffle furnace; 8) slab, water-cooled; 9) guide tube; 10) thermo-couple; 11) EPD-52 potentiometer.

Weighed samples of boron phosphide (0.2 g) and gallium and indium phosphides (0.3 g) were placed in a quartz crucible 5 15 mm high with a 12 mm diameter which was suspended in a vertical muffle furnace 7 on a platinum filament 4 set in a guide tube 9 and connected with thermo-balances 3 (Fig. 1).

The change in the sample's weight was noted over fixed periods of time without removing it from the heating zone. The sample was oxidized to a constant weight, which indicated that the oxidation of the sample was complete for the given temperature. After the experiment was finished, the sample was removed from the heating zone and the reaction products were carefully separated from the remaining phosphides and checked by chemical and x-ray analysis. The data for the oxidation of the boron, gallium and indium phosphides in air are given in Tables 1 and 2 and shown graphically in Figs. 2-5. /39

The results showed that the microcrystalline boron phosphide is stable to oxidation up to 600°C, gallium phosphide is stable to 700°C and indium phosphide to 700°C. It should be noted that enlargement of /40

TABLE 1

RESULTS OF THE OXIDATION OF BORON, GALLIUM AND INDIUM PHOSPHIDES IN AIR ($Y = \Delta Q/V$, g/cm³, where ΔQ is the change in weight in g and V is the volume of the phosphide, cm³, τ is the oxidation time in min.)

Phosphide	Temperature, °C	Oxidation Equation	Remarks
BP	600	$Y^2 = 2,34 \cdot 10^{-6} \tau$	Particle size - 2-3 μ
	700	$Y^{2,1} = 2,3 \cdot 10^{-6} \tau$	
	800	$Y^2 = 3,6 \cdot 10^{-6} \tau$	
	900	$Y^{2,5} = 6,5 \cdot 10^{-5} \tau$	
CaP	700	$Y^{1,7} = 2,7 \cdot 10^{-7} \tau$	Particle size - 7-10 μ
	750	$Y^{1,7} = 3,63 \cdot 10^{-7} \tau$	
	800	$Y^2 = 1,32 \cdot 10^{-6} \tau$	Time period - 0-14 min.
	900	$Y^{2,7} = 2,3 \cdot 10^{-6} \tau$	
	950	$Y = 7,1 \cdot 10^{-2} \tau$	
InP	700	$Y^{2,5} = 1,0 \cdot 10^{-4} \tau$	Particle size - 7-10 μ
	800	$Y^{2,5} = 1,78 \cdot 10^{-5} \tau$	
	850	$Y^{2,3} = 5,87 \cdot 10^{-5} \tau$	Time period - 0-36 min.
	900	$Y = 4,7 \cdot 10^{-2} \tau$	

TABLE 2

RESULTS OF THE ANALYSIS OF THE PHOSPHATES
AND THE VALUES OF THE ACTIVATION ENERGY
FOR THE PHOSPHATE-FORMATION PROCESS

Phosphate	Composition, weight %		Lattice Parameters	Activation Energy, cal/mole
	P	Me		
BPO ₄	29,7	10,6	$a = 4,33; c = 6,34$ $a = 4,92; c = 6,87$ —	24 500
CaPO ₄	18,2	43,4		24 750
InPO ₄	26,3	55,2		31 700

the phosphide particles results in a greater stability towards oxidation, which means that the boron, gallium and indium phosphides can be considered as valuable semiconducting materials.

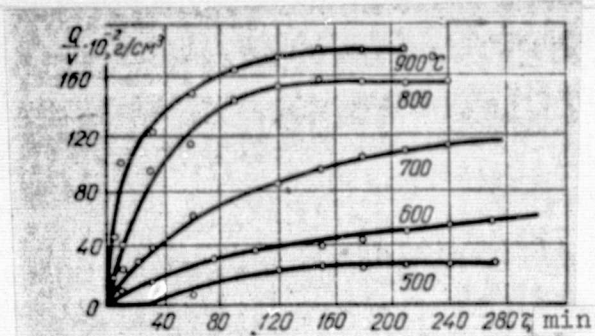


Fig. 2. Oxidation isotherms for boron phosphide in air.

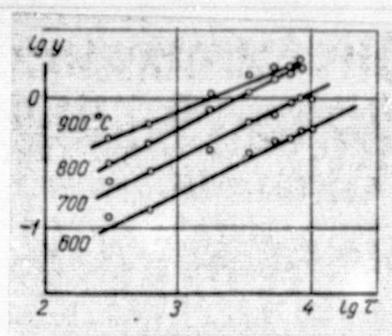


Fig. 3. Results of the oxidation of boron phosphide in the coordinates $\log y - \log \tau$

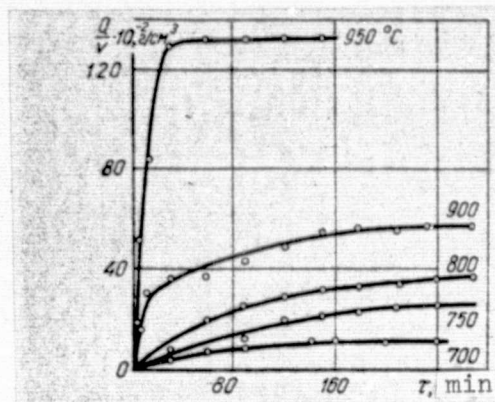


Fig. 4. Isotherms for the oxidation of gallium phosphide in air.

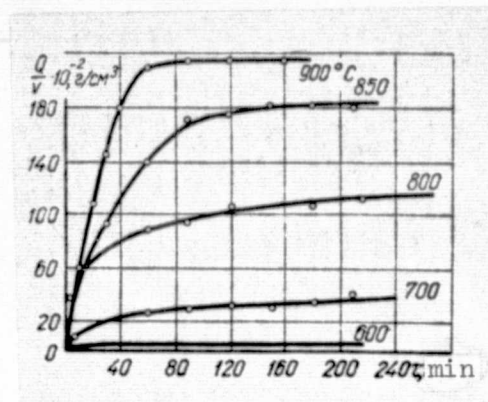


Fig. 5. Isotherms for the oxidation of indium phosphide in air.

The kinetic curves obey a parabolic rule $Y^n = K\tau$ for the oxidation of the phosphides in the following temperature ranges: 600-900° for boron phosphide, 700-850° for gallium phosphide, and 700-850° for indium phosphide.

Because of the intensive reaction at 900 and 950°C for gallium and indium phosphide, respectively, the process for the formation of the reaction products is given by a linear relationship. The rate of the consecutive stages of the process are controlled by the diffusion of the reaction components through a layer of the phosphates which are formed. The chemical and x-ray methods showed that the final products of the oxidation reaction are the phosphates.

Since the oxidation of the boron, gallium and indium phosphide was studied on powdered samples, the results cannot be reduced to rigorous quantitative relationships and the given equations are

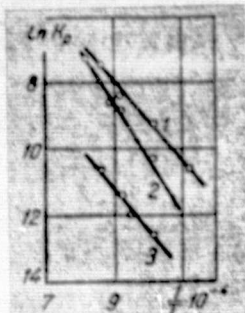


Fig. 6. The temperature dependence of the rate constant for the oxidation of boron phosphide (1), gallium (2), and indium phosphide (3) in air.

empirical. The fact that in the majority of cases the quadratic parabolic oxidation rule, which is characteristic for compact materials and alloys, is not obeyed is also explained by this. However, the data allow us to evaluate the onset of oxidation for the phosphides and determine the final products. The results can be used

to determine the possibility of producing these phosphides by tangential methods and in developing methods for the chemical analysis of these compounds and their alloys.

CONCLUSIONS

1. Microcrystalline boron phosphide is stable towards oxidation at temperatures up to 600°C. Gallium and indium phosphide are stable up to 700°C.
2. The kinetic curves for the oxidation of the phosphides obey a parabolic law for temperatures of 600-900°C for boron phosphide, 700-900°C for gallium phosphide, and 700-850°C for indium phosphide.
3. Chemical and x-ray analysis showed that the final oxidation products are the phosphates.

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RESISTANCE OF REFRACTORY MATERIALS OF SILICON NITRIDE- SILICON CARBIDE TO HIGH TEMPERATURE OXIDATION

/42

I. N. Godovannaya and O. I. Popova*

Silicon nitride and carbide are promising materials for refractories. They have a good resistance to the action of mineral acids and bases, a high melting point, and high thermal stability [1].

The resistance of refractory materials based on silicon carbide and nitride to oxidation was studied for different ratios of the components¹.

The sample (0.5 g) was evenly distributed in a combustion boat and placed in the porcelain tube of a Mars furnace. The furnace temperature was rigorously controlled with a thermocouple. The flow rate of the oxygen was constant in all of the experiments. The oxygen flow was passed through the reaction zone for a fixed period of time and the amount of oxidized carbon was determined by the absorption-gas exchange method [1]. The amount of oxidized carbon was determined from the formula

$$C_{\text{oxidized}} = \frac{(C_{\text{total}} - C_{\text{free}}) \cdot 100}{C_{\text{bound}}}$$

where C_{total} is the amount of oxygen burned off in the given time period in %, C_{free} is the amount of free carbon in the sample in %, and $\% C_{\text{bound}}$ is the amount of carbon bound in the form of SiC in %.

The initial silicon carbide and silicon nitride was oxidized in addition to the samples containing silicon carbide and nitride (Table 1).

It follows from the data shown in Figs. 1-6 that at 1000°C all

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¹The samples were prepared in the Section on Refractory Compounds, Institute of Material Behavior Problems, AN Ukr SSR by V. K. Kazakovyí.

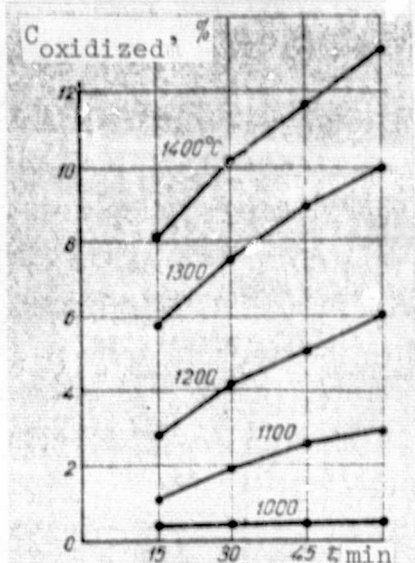


Fig. 1. Oxidation of the initial silicon carbide as a function of time over a range of temperatures.

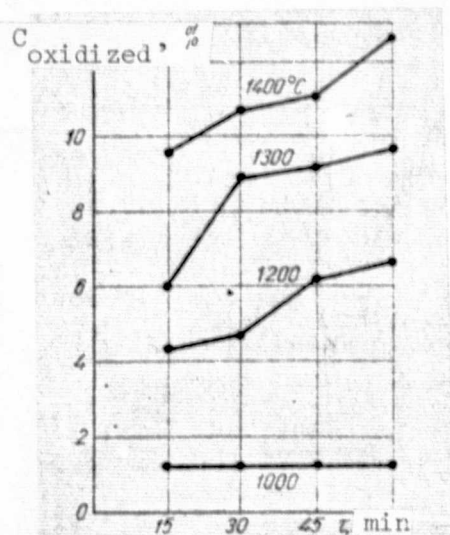


Fig. 3. Dependence of the degree of oxidation on time over a range of temperatures for alloy No. 2 which contains 15.2% silicon carbide and 84.8% silicon nitride.

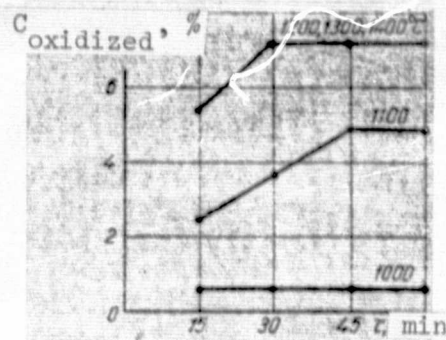


Fig. 2. Dependence of the degree of oxidation on time for different temperatures for the alloy No. 1 which contains 10.4% silicon carbide and 89.6% silicon nitride.

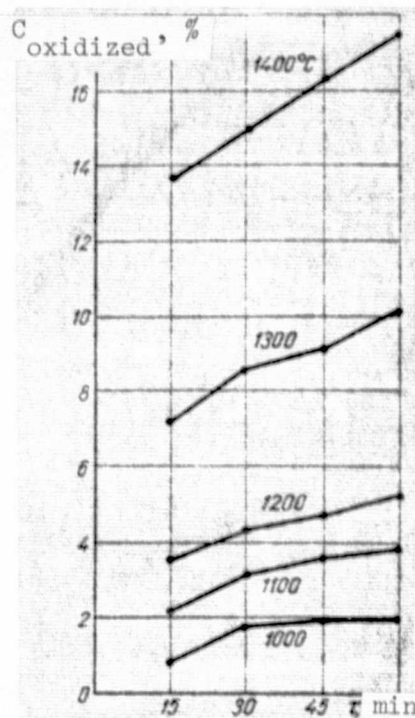


Fig. 4. Dependence of the degree of oxidation on time at various temperatures for alloy No. 3 which contains 32.4% silicon carbide and 67.6% silicon nitride.

of the samples are slightly oxidized (the straight line is parallel to the abscissa). At higher temperatures the degree of oxidation increases with time although the oxide film still protects both the alloys and the initial silicon carbide.

CHEMICAL COMPOSITION OF SAMPLES
WEIGHT IN %

Sample No.	SiC	Si ₃ N ₄	C _{free}	C _{bound}
1	10,4	89,6	0,11	3,12
2	15,2	84,8	0,21	4,55
3	32,4	67,6	0,11	9,73
4	40,3	59,7	0,13	12,10

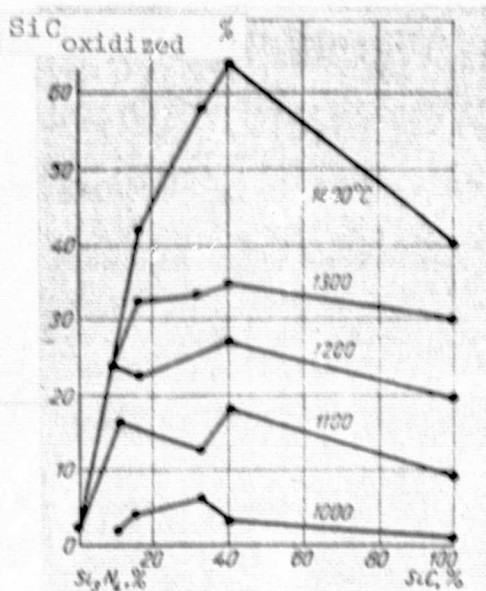


Fig. 6. Dependence of the oxidation of the silicon nitride on the composition for various temperatures for a period of 1 hr.

in the alloys which contain silicon nitride.

The greatest difference in the oxidation of the alloys and of the initial products is found at 1400°C and for a ratio of the components of Si₃N₄ : 1.8 SiC. It is apparent that at this ratio compounds are formed with a maximum instability to oxidation.

Thus, the stability of the refractory alloys which consist of silicon carbide and silicon nitride towards oxidation decreases somewhat as compared with the initial silicon carbide and nitride.

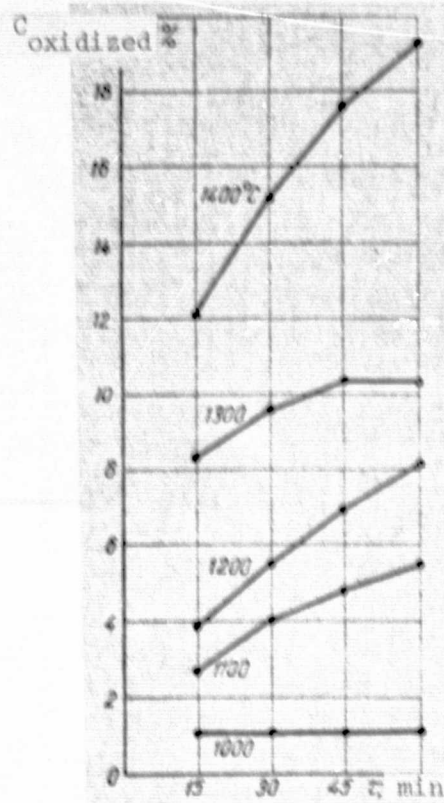


Fig. 5. Dependence of the degree of oxidation on time for various temperatures for alloy No. 4 containing 40.3% silicon carbide and 59.7% silicon nitride.

If we compare these data with the data on the oxidation of the initial silicon carbide, it appears that the oxidizability of the silicon carbide increases somewhat

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METHODS OF PREPARATION AND THE CHEMICAL STABILITY
OF THE HYDRIDES OF THE GROUP IV AND V
TRANSITION METALS

M. M. Antonova*

In terms of their bonds and physical and chemical properties, the hydrides of the Group IV and V transition metals belong to the group of "metallic" hydrides; however, there are almost no precise data on the relative properties of the hydrides in the literature. Their study was hindered by their thermal instability, the unique absorption of hydrogen and the lack of methods for producing the hydrides in compact state. Recently the experimental difficulties that were encountered in studying the hydrides have been overcome to a large extent, which has resulted in the appearance of a large number of experimental and theoretical studies of the transition metal hydrides.

The transition metal hydrides can be produced in the form of powders by three rather simple methods. The first is the direct reaction of the metal with gaseous hydrogen. In this, metals and hydrogen with a high degree of purity are used. The hydrogen is most often produced by the decomposition of the titanium, zirconium and uranium hydrides [7]. The conditions for producing the transition metal hydrides are given in Table 1.

In the hydrogenation of the compact metal, a product is obtained in the form of fine pieces of the hydride which are readily crushed into a powder. The specific volume of the hydride increases by 15-25% /46 as compared with the starting metal. The resulting hydride is slightly duller than the starting metal.

The second widely used method for producing the transition metal hydrides is the reduction of the oxides of the refractory metals by hydrides and metals. Calcium hydride CaH_2 is used most often for this

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TABLE 1
CONDITIONS FOR PRODUCING THE GROUP IV AND V HYDRIDES (2)

Hydride	Hydrogenation Temperature, °C	Hydrogenation Time, min.	Chemical composition of the hydride, wt. %	
			Metal	Hydrogen
TiH ₂	400	30	95,92	4,02
ZrH ₂	600	30	97,86	2,14
HfH ₂	800	30	98,90	1,10
VH _{0,9}	800	120	98,25	1,75
NbH	800	120	98,44	1,06
TaH _{0,7}	800	60	99,12	0,38

purpose [5,6]. The oxides are loaded layer-wise with the calcium hydride into an iron shell and then placed in a furnace where the reduction takes place in a hydrogen atmosphere.

The temperature of the production process fluctuates in the 900-1100°C range. The resulting hydride is washed with a weak solution of HCl to remove the calcium oxide mixed with it. The dihydrides of titanium and zirconium and the monohydrides of vanadium, niobium and tantalum are produced in this way. The first two methods have been developed quite well for producing the hydrides commercially.

The third method for producing the hydrides from solutions is as yet not developed well enough. It consists either of treating the metal powder with acids (hydrofluoric, hydrochloric) [9,11] or a reaction of phenylmagnesium bromide with the metal chlorides in an ether solution [1]. In the first case, a mixture of crystals of the hydride and of the metal deposits out which is almost impossible to separate because of the lack of information on the hydrides. The size of the crystals depends on the concentration of the acid that is used. The hydrides produced from the phenylmagnesium bromide have not as yet been isolated in the free state from the etherate state. In trying to remove the ether, the hydrides are decomposed into the metal and hydrogen. Therefore, the method for producing the hydrides from solutions needs a great deal of refinement to be used on a wide scale.

TABLE 2
COMPOSITION OF THE HYDRIDES USED TO STUDY THE CHEMICAL PROPERTIES

Hydride	Composition of the hydride by chemical analysis, wt. %		Particle size of the powder
	Metal	Hydrogen	
TiH _{1.83}	96.7	3.03	15
ZrH ₂	97.51	2.00	5-6
NbH	98.70	1.06	10-15

Compact samples of titanium and zirconium hydride were first produced just recently [3,12] by means of reaction sintering. The method is only applicable for the exothermal reactions and it consists of the following. During the hydrogenation reaction, which is carried out at the temperature for the maximum absorption of hydrogen, a large amount of heat is evolved which heats the metal being hydrogenated to 900-1000°C, causing its plasticity to increase, and it becomes sintered because of the heat of reaction, with simultaneous hydrogenation. The resulting hydrides have a density up to 80% of the theoretically calculated value and, upon breaking, it has the appearance of a solid metal with a clearly expressed metallic sheen. /47

The chemical composition of the transition metal hydrides has not been studied at all (if we do not consider the brief qualitative description given by Herd [8]). Therefore, studies were initiated on determining the chemical properties of the hydrides, particularly the oxidation of the hydrides in a stream of oxygen and the chemical stability is some widely used reagents. The data given here refer to some of the studies of the powdered transition metal hydrides. The hydrides that were used were prepared by the direct reaction of the powdered metals with hydrogen. The composition of the hydrides is given in Table 2.

The rate of oxidation of the titanium, zirconium and niobium hydrides was studied by burning a sample of the hydride weighing about 1 g in a stream of oxygen in a quartz reactor placed in a resistance

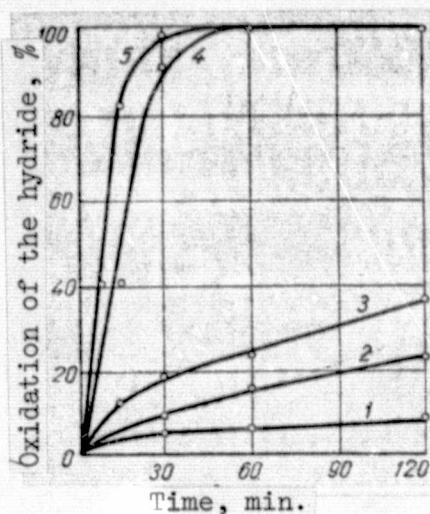


Fig. 1. Kinetic curves for the oxidation of titanium hydride: 1) at 400°C; 2) at 500°C; 3) 550°C; 4) 600°C; 5) 700°C.

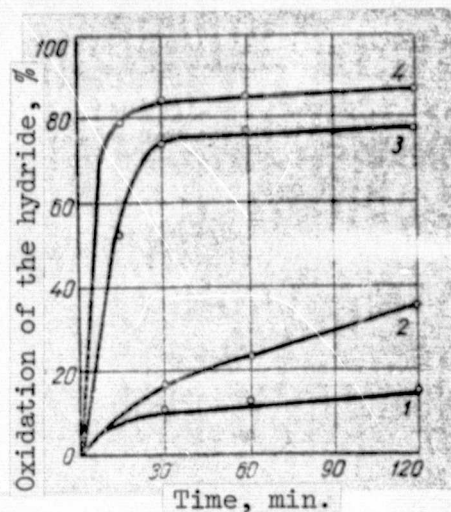


Fig. 2. Kinetic curves for the oxidation of zirconium hydride: 1) at 400°C; 2) 450°C; 3) 470°C; 4) 500°C.

furnace, and determining the amount of water vapor formed in the oxidation gravimetrically and weighing the sample before and after the experiment. The degree of oxidation of the hydride was determined both from the amount of water vapors that were collected and from the increase in weight for the oxidized hydride. The hydride powders were oxidized for two hours at 300-700°C. In order to get comparable results, it was assumed that combustion was 100% for all three hydrides in calculating the amount of oxidized hydrogen and the total hydrogen concentration in the initial hydride. The results of the oxidation are shown in Figs. 1-3. The rule for the oxidation was determined from the shape of the resulting oxidation curves and the temperature dependence was calculated for the oxidation constant. /48

The experimental results show that the oxidation of the titanium hydride begins at 500-550°C, for zirconium hydride it begins at 450-470°C, and at 300-350°C for niobium hydride. An analysis of the kinetic curves for the oxidation of the hydrides shows that the oxidation rule changes as the oxide film grows. The formation of each oxide has its own oxidation rule. As the oxide is converted to the higher oxide, the oxidation rule acquires the shape of a quadratic parabola, indicating that the oxidation is controlled by the diffusion of the oxygen through the film of the higher oxide. The kinetic curves

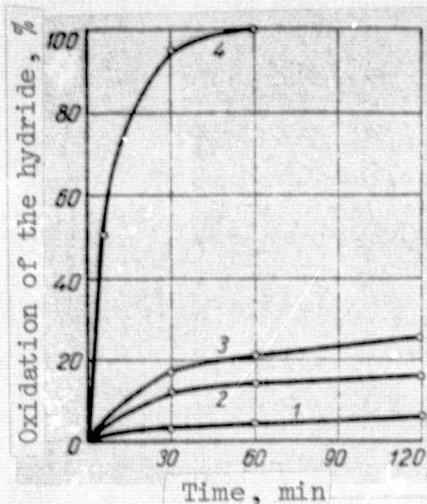


Fig. 3. Kinetic curves for the oxidation of niobium hydride: 1) at 300°C; 2) 350°C; 3) 400°C; 4) 500°C.

The stability of these hydrides in different media was studied at room temperature and with boiling. In studying the stability of the hydrides at room temperature, a sample of the hydride weighing 0.2 g was placed in a beaker and 100 ml of the reagent was added and kept for eight hours with periodic stirring. In studying the stability with boiling, the sample was placed in a tapered flask connected to a reflux condensor by a ground glass joint and the mixture was boiled for eight hours. The insoluble residue was filtered off on a No. 4 Schott filter and the percent of undissolved metal was determined from the weight loss. The metal which is dissolved was determined by the cupferron method (Table 3).

The zirconium hydride is completely decomposed by concentrated sulfuric acid and by hydrofluoric acids of all concentrations with the vigorous evolution of fine bubbles of hydrogen. The reaction is less vigorous with orthophosphoric acid and only takes place with boiling, in which case the evolution of hydrogen cannot be observed visually. The zirconium hydride dissolves in the rest of the mineral acids only slightly. Upon dissolving, the hydride zirconium salts of the corresponding acids are formed. No hydrolysis of the salts was observed upon diluting the acids. The zirconium hydride dissolves completely only in mixtures with hydrofluoric acid.

for the oxidation of the hydrides, calculated from the weight of entrapped water vapor and the increase in weight, differ quantitatively and qualitatively from one another. It may be assumed that the oxidation of the hydrogen precedes its decomposition with the subsequent separate oxidation of metal and of the hydrogen which is evolved. This assumption is confirmed tangentially by the data on the dissociation of these hydrides in a vacuum [4].

TABLE 3
STABILITY OF ZIRCONIUM HYDRIDE IN CHEMICAL SOLUTIONS

Medium	Temperature, °C	Residue, %	Dissolved material, %	Metal in solution, %
H ₂ O	100	100	—	—
HCl Concentrated	108	96.4	3.60	3.60
HCl (1:1)	108	95.4	4.60	4.50
HNO ₃ Concentrated	110	97.8	2.20	2.25
ная HNO ₃ (1:1)	110	97.8	2.20	2.20
H ₂ SO ₄ Concentrated	280	—	100	100
ная H ₂ SO ₄ (1:1)	136	68.95	31.05	30.95
HF Concentrated	25	—	100	100
H ₃ PO ₄ Concentrated	100	—	100	100
H ₂ O ₂ (33%)	100	99.35	0.65	0.65
NH ₄ OH	25	100	—	0.37
NaOH (10%)	110	102.2	—	30.7
KOH (10%)	105	100.8	—	3.05
Acetic acid	100	100	—	1.41
Tartaric acid	25	100	—	—
Oxalic acid	100	93.72	6.28	6.27
CCl ₄	25	100	—	—
Acetone	25	100	—	—
Ethyl alcohol	25	100	—	—
HF + HNO ₃ (1:1)	25	—	100	100
HNO ₃ + H ₂ SO ₄ (1:1)	100	85.8	14.2	14.15
HNO ₃ + H ₂ O ₂ (1:1)	100	97.7	2.3	3.10

As a rule, an increase is found in the residue for the dissolution of zirconium hydride in alkalis, as compared with its initial weight, and significant amounts of zirconium are observed in the solution. This may be explained by the formation of zirconates whose solubility depends greatly on the medium's acidity and therefore part of the zirconium goes into solution and the weight of the residue increases because of the formation of an insoluble salt. The external appearance of the powder does not change in its reaction with the alkali. /50

Zirconium hydride does not dissolve to any great extent in organic acids and solvents. A conversion of the zirconium into solution is only found in oxalic acid (Table 4).

Titanium hydride is readily soluble in hydrochloric, sulfuric and hydrofluoric acids of all concentrations, even in the cold. The

TABLE 4
STABILITY OF TITANIUM HYDRIDE IN CHEMICAL SOLUTIONS

Medium	Temperature, °C	Residue, %	Dissolved material, %	Metal in solution, %
H ₂ O	100	100	—	—
HCl Concentrated	100	—	100	100
HNO ₃ Concentrated	25	59.8	40.2	40.2
H ₂ SO ₄ Concentrated	280	—	100	100
H ₂ SO ₄ (1:1)	120	—	100	100
HF Concentrated	25	—	100	100
H ₃ PO ₄ Concentrated	70	—	100	100
H ₃ PO ₄ (1:1)	100	3.97	96.03	88.70
NH ₄ OH	100	108.5	—	0.44
KOH (10%)	100	112.2	—	—
NaOH (10%)	100	111.8	—	43.8
Tartaric acid	100	100	—	—
Acetic acid	100	100	—	—
Oxalic acid	100	5.58	96.42	97.2
CCl ₄	25	100	—	—
Acetone	25	100	—	—
Dichloroethane	25	100	—	—
HF + HNO ₃ (1:1)	25	—	100	100
H ₂ SO ₄ + HNO ₃ (1:1)	100	—	100	100

dissolution is greatly accelerated for boiling. Titanium hydride also dissolves completely in orthophosphoric acid. The dissolution in concentrated sulfuric acid takes place very unusually: first there is a vigorous reaction with the evolution of a gas and the formation of a white, powdered, very fine precipitate which, upon further boiling in sulfuric acid, dissolves completely to form a colorless, transparent solution. This kind of dissolution is also observed in a mixture of sulfuric acid and nitric acid. It may be assumed that in this case, TiO₂ (or TiSO₄)₂ is formed, which then dissolves with the formation of titanylsulfate TiOSO₄, which exists in acid solutions. In order to explain the composition of the white precipitate, an attempt was made to separate it from the solution, which was not found possible. After filtering the precipitate on a Schott filter and washing it with hot distilled water, the precipitate dissolved completely in the water. This allows us to exclude TiO₂ as the material, and leads to the conclusion that in the initial period of dissolving titanium hydride in concentrated sulfuric acid, Ti(SO₄)₂, which has a limited solubility, is formed which, upon further boiling, is converted into the readily soluble titanyl sulfate TiOSO₄.

/51

TABLE 5
STABILITY OF NIOBIUM HYDRIDE IN CHEMICAL SOLUTIONS

Medium	Temperature, °C	Residue, %	Dissolved material, %	Metal in solution, %
H ₂ O	100	100	—	—
HCl Concentrated	108	61.1	38.9	38.8
HCl (1:1)	108	96.8	3.2	2.96
HNO ₃ Concentrated	110	99.4	0.6	0.5
HNO ₃ (1:1)	100	98.8	1.2	1.32
H ₂ SO ₄ Concentrated	280	—	100	100
H ₂ SO ₄ (1:1)	136	43.35	56.65	57.1
H ₃ PO ₄ Concentrated	100	5.39	94.61	94.70
H ₃ PO ₄ (1:1)	100	69.2	30.8	30.8
HF Concentrated	25	—	100	100
KOH (10%)	100	27.8	72.2	85.0
NaOH (10%)	100	197.5	—	40.2
H ₂ O ₂ (33%)	100	92.9	7.1	7.15
Tartaric acid	100	96.8	3.2	3.25
Acetic acid	100	100	—	—
Oxalic acid	100	60.6	39.4	39.5
CCl ₄	25	100	—	—
Acetone	25	100	—	—
Dichloroethane	25	100	—	—

A colorless solution is formed in sulfuric and orthophosphoric acids indicating the presence of the tetravalent Ti^{4+} ion. In all of the rest of the inorganic acids and their mixtures, trivalent titanium is formed in solution (violet solution). Among the organic acids and solvents that were studied, only oxalic acid dissolves titanium hydride in any quantity.

The character of the dissolution of titanium hydride in alkalis is the same as that for zirconium hydride. In this case, titanates are formed which are not very soluble. They precipitate out and form a mixture with the initial powdered hydride. /52

Niobium hydride has a lower solubility in acids than the hydrides of titanium and zirconium. Even in concentrated sulfuric acid, it only dissolves by boiling for 1.5 hrs. This indicates that in solution niobium has a more amphoteric nature and has a greater tendency to form salts with the alkalies. The hydride dissolves completely in sodium hydroxide solutions; however, the resulting salt hydrolyzes

upon dilution of the solution to form a white, fine-crystal precipitate of the hydroxide which is not readily soluble in either acids or alkalis. The niobium hydride behaves in the same way as the hydrides of titanium and zirconium with respect to organic acids.

As a result of these studies on the stability of the titanium, zirconium and niobium hydrides to chemical reagents, we can see that their stability is identical with the stability of the initial metals which, however, can only be stated qualitatively since there is no experimental information on the stability of the metal powders under these conditions.

Specifically, this study showed that the dissolution of the hydrides in chemical reagents cannot be reduced to a scheme of "decomposition of the hydride to the metal and hydrogen followed by the dissolution of the metal in the solution." An analysis of the insoluble residue for metal and hydrogen shows that the composition of the hydride does not remain constant during the reaction. It changes, but the complete absence of hydrogen was not observed in a single case. The amount of hydrogen which remains in the residue is different for the dissolution of the hydride in various reagents; however, it was not possible to find any rule for its quantitative amount.

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CHEMICAL ANALYSIS OF THE PRODUCTS FROM THE REACTION OF BORON WITH ARSENIC AND PHOSPHORUS

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The phosphides and arsenides of boron are refractory compounds which can be used in semiconductor technology. Great interest has been evidenced in the synthesis of these compounds recently, both abroad and here [10]; however, there are few works in the literature on their chemical analysis [1,9,12].

A study of the processes which take place during the reaction of boron with phosphorous and arsenic allowed methods to be developed for the synthesis of boron phosphide powders [3], boron arsenide BAs, and arsenic hexaboride B_6As powders [6,4], as well as for the solid solutions of BAs - BP in the ternary system B-As-P [5]. The products which are formed were determined by chemical, spectroscopic, and x-ray-phase methods.

In this article, methods are given for the analysis of the products from the reaction of boron with arsenic and phosphorus as well as for the powders with a ternary B-As-P composition. The starting materials for the synthesis were amorphous boron, red phosphorus, and crystalline arsenic (Table 1). The reaction of solid boron with phosphorus and arsenic vapors was carried out under heterogeneous conditions.

The reaction of amorphous boron with arsenic was studied in a vertical furnace in quartz crystals sealed under vacuum by varying the composition of the starting mixtures over a wide range. The temperature in the furnace was $700-760^{\circ}$ and $1100^{\circ}C$, depending on the composition of the mixture. The results of the x-ray phase [4] and chemical [7] analyses of the reaction products showed that boron forms

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TABLE 1
SPECTROSCOPIC ANALYSIS OF THE STARTING MATERIALS

Material analyzed	Impurities, wt. %					
	Si	Te	Mg	Pb	Al	Cu
Boron	$3 \cdot 10^{-3}$	$1,3 \cdot 10^{-3}$	$3 \cdot 10^{-4}$	$5 \cdot 10^{-4}$	$2,7 \cdot 10^{-4}$	$4,5 \cdot 10^{-4}$
Phosphorus	$3,6 \cdot 10^{-4}$	$1,8 \cdot 10^{-4}$	—	—	$1 \cdot 10^{-4}$	$1 \cdot 10^{-4}$
Arsenic	10^{-5}	10^{-5}	—	—	10^{-5}	—

two chemical compounds with arsenic: BAs and B_6As . In the presence of an excess of arsenic as compared with the stoichiometric amount (> 50 at. %) and at $700-760^\circ C$, a black powder of BAs was formed which was readily separated from the arsenic by distilling off the latter at $400^\circ C$ in the "cold" part of the ampule. At $1100^\circ C$ a yellow-brown powder B_6As is formed from the reaction of boron with arsenic taken in an amount less than 50 at. %. This powder is single phase or it contains an excess of boron or arsenic depending on the composition of the starting mixture. The hexaboride was isolated from the excess boron by boiling in nitric acid in which the B_6As is almost insoluble. It was separated from the excess arsenic by distillation without opening the ampule as in the case of the BAs .

/54

The pure hexaboride can be produced from the boron arsenide by heating the latter at $1100^\circ C$. The BAs loses part of its arsenic because of thermal dissociation and is converted to B_6As . The arsenic which is given off is distilled into the "cold" part of the ampule.

The compounds that have been obtained for boron with arsenic have a high chemical stability. A check of the solubility of B_6As in some acids (Table 2) showed that none of the given acids or their mixtures dissolve the hexaboride completely.

For prolonged boiling, the boron arsenide dissolves almost completely in nitrore; however, the presence of an insoluble residue and the prolonged boiling time (8-10 hrs.) make this method undesirable for analytical purposes.

The method of fusion was used to convert the material into a

TABLE 2

CHEMICAL STABILITY OF B_6As WHICH DISSOLVES (in wt. %)
IN SOME ACIDS (sample weight 100 mg, solvent - 20 ml)

Medium	Boiling for 2.5 hrs.	In the cold for 24 hrs.
HNO_3 ($d = 1.4 \text{ g/cm}^3$)	28.7	35.0
$HNO_3 + H_2O_2$ (1:1)	43.0	36.1
$HNO_3 + H_2O_2$ ($d = 1.19 \text{ g/cm}^3$)	2.9	2.5
$HCl + HNO_3$ (3:1)	41.1	48.0
H_2SO_4 ($d = 1.8 \text{ g/cm}^3$)	8.5	5.0

soluble state. For this, 0.1 g of the powder sample was fused in a nickel crucible with 1 g of alkali and 0.5 g of sodium peroxide. At first the alkali was fused to remove the moisture and then it was cooled, the sample was added, and the mixture was again fused to lower the sample's activity. After solidifying in the crucible, the sodium peroxide was added and it was carefully fused, beginning by heating the crucible walls, in a low burner flame. As the mixture is fused, the flame is increased and the heating is continued for 10 min. After leaching the alloy with hot water, the boron and arsenic were dissolved in the form of the borate and arsenate. The solution was boiled for 1 hr. in a flask equipped with a reflux condenser to decompose the peroxide and then the mixture was filtered and transferred to a 200 ml volumetric flask.

/55

The arsenic was determined iodometrically. The presence of boron does not interfere with the determination. For this, 10 ml of (1 : 1) H_2SO_4 was added to a 50 ml aliquot along with a few drops of a permanganate solution until a rose color was obtained. The excess permanganate was decomposed by the addition of 2 ml of alcohol and boiling. After the peroxide residues were decomposed in this way, 40 ml of hydrochloric acid ($d = 1.19 \text{ g/cm}^3$) and 0.5-1 g of potassium iodide were added to the mixture. The iodine which is released is titrated immediately with a 0.02 N solution of thiosulfate until the solution has no color. The titration is completed without starch, since the latter gives unreliable colors in strong acids. After 20 minutes, the solution is titrated to completion if it takes on a

yellow color during standing in the dark. A blank is run with the same amounts of reagents.

The boron is determined on another portion of the solution by titration with an alkali in the presence of mannite. The end point is observed visually using phenolphthalein or potentiometrically. For boron concentrations in the sample which correspond to the composition BAs (12.72 weight % boron and 87.28 weight % arsenic), the titration was carried out as follows: After adding hydrochloric acid to a 50 ml aliquot to get a rose color with methyl red and boiling for 5-7 min. to remove the carbon dioxide and then cooling rapidly in running water, several drops of phenolphthalein are added to the solution to indicate the neutral point upon the addition of a 0.1 N solution of NaOH. After adding 1-2 g of mannite, the mixture was titrated with the alkali until a consistent rosy color was achieved which does not disappear upon the addition of more mannite.

If the boron concentration corresponds to the composition of arsenic hexaboride (46.43 weight % boron - 53.57 weight % arsenic), the boron concentration determined in this way is somewhat low because of the partial neutralization of the boric acid in establishing the neutral point with respect to phenolphthalein. Therefore, in analyzing the arsenic hexaboride, the boron is determined somewhat differently.

The neutral point is established with methyl red, which corresponds to the neutralization of strong hydrochloric acid and the first step of the weak arsenic acid. Then mannite is added and phenolphthalein are added and the solution is titrated to the red color.

Since the arsenic acid is titrated to the second stage along with the boric acid for titration using the phenolphthalein end point, a correction was introduced in the calculation for boron for the arsenic concentration, which is calculated on the basis of the iodometric determination of the arsenic which was done on a separate portion of the solution. The amount of thiosulfate used in the titration was converted to the appropriate volume of alkali. The latter was subtracted from the total amount of alkali used in determining

TABLE 3

DETERMINATION OF BORON IN THE PRESENCE OF ARSENIC
FROM AN ARTIFICIAL MIXTURE OF BORIC AND ARSENIC ACIDS

Boron taken, mg	Arsenic added, mg	Correction factor, mg	Boron found, mg	Error in determination	
				mg	%
8.0	—	—	8.0	0.0	0.0
8.0	—	—	8.0	0.0	0.0
8.0	—	—	8.0	0.0	0.0
8.0	9.8	1.20	8.1	+ 0.1	1.2
8.0	9.8	1.20	8.0	0.0	0.0
8.0	9.8	1.20	8.1	+ 0.1	1.2
16.0	—	—	16.0	0.0	0.0
16.0	—	—	15.9	- 0.1	0.6
16.0	24.5	2.29	15.9	- 0.1	0.6
16.0	24.5	2.99	16.1	+ 0.1	0.6

boron.

The results for determining boron from synthetic mixtures with arsenic are given in Table 3. The fixed pH method was used to determine boron potentiometrically which allows interferences due to the presence of weak acids to be avoided [1,2]. For this purpose, the pH of the solution, after boiling and cooling, was set at 6.9 on the LP-58 potentiometer. Then the mannite was added and the solution was titrated with 0.1 N alkali to a pH of 6.9. The alkali titer was determined with twice recrystallized boric acid under the same conditions. This method was checked on synthetic mixtures of boric acid with arsenic acid and also with a mixture of phosphoric and arsenic acids (Table 4). The error in determining boron does not exceed ± 0.4 relative %.

In calculating the bound boron and arsenic in the hexaboride powders, the concentration of free, unreacted elements was taken into account, which were determined after boiling the sample in hydrogen peroxide with the addition of a few drops of nitric acid.

Gueilleron and Thevenot [12] determined the ratio B : As = 6.2 : 6.3 for this compound by chemical analysis which allowed them to choose between the formulas B_6As and $B_{13}As_2$.

TABLE 4
POTENTIOMETRIC DETERMINATION OF BORON IN THE PRESENCE OF
PHOSPHORUS AND ARSENIC

Used, in mg			Boron found, mg	Relative error, %	Boron used, %	Boron found, %	Absolute error, %
Boron	Phospho- rus	Arsenic					
27.1	—	—	27.11	+ 0.04	100	100.04	+ 0.04
27.1	—	—	27.13	+ 0.11	100	100.11	+ 0.11
27.1	—	—	27.05	- 0.19	100	99.82	- 0.19
27.1	36.4	—	27.45	+ 1.30	42.68	43.23	+ 0.55
27.1	36.4	—	27.09	- 0.04	42.68	42.67	- 0.01
27.1	36.4	—	27.13	+ 0.11	42.68	42.73	+ 0.05
27.1	—	37.3	27.06	- 0.15	42.08	42.02	- 0.06
27.1	—	37.3	27.10	0.0	42.08	42.08	0.0
27.1	36.4	37.3	27.22	+ 0.44	26.88	27.00	+ 0.12
27.1	36.4	37.3	27.30	+ 0.74	26.88	27.08	+ 0.20
13.55	29.85	29.78	13.47	- 0.60	18.69	18.58	- 0.11
13.55	29.85	29.78	13.50	- 0.40	18.69	18.62	- 0.07
13.55	29.85	29.78	13.64	+ 0.60	18.69	18.82	+ 0.13
13.55	29.85	29.78	13.49	- 0.40	18.69	18.61	- 0.08

Remarks: The average error for the determination, %:
relative ± 0.36 , absolute - ± 0.12 .

In analyzing several samples of arsenic hexaboride produced in our laboratory, a ratio of B : As close to 6 : 1 was found and, therefore, the formula B_6As was assigned to it. This composition was confirmed by x-ray analysis [4].

The composition of the black powder which is obtained at 700-760°C, according to the results of chemical analysis, is close to the stoichiometric composition BAs . In studying the reactions of boron with phosphorus, the kinetics were studied for the process [3]. The experiments were made in a two-zone, horizontal furnace in which the constant temperature for the phosphorus zone was 400°C and the variable temperature for the boron zone was 1000-1150°C. The boron and the phosphorus (in the stoichiometric ratio) were placed in a quartz combustion boat and placed at opposite ends of the ampule which was evacuated to 10^{-5} mm and sealed. After the appropriate time, the ampule was taken from the furnace and the phosphorus which had not reacted was condensed in the "cold" zone at 800°C. After opening the ampule, the combustion boat containing the boron was weighed and the increase in weight was used to calculate the reaction yield. Since

/57

the reaction does not go to completion, the powder that was obtained was analyzed chemically. The experiments showed that the yield of BP depends on the reaction surface as well as on the time and temperature. The boron phosphide which is obtained in the form of a crystalline, yellow-brown powder, was separated from the unreacted boron by boiling in a mixture of concentrated HNO_3 with H_2O_2 or in aqua regia in which solvents the boron phosphide is insoluble.

The chemical stability of boron phosphide has been noted by many authors [1,10,13]. Andreyeva and Yefremov [1] used chlorination in an isolated system at 550°C to decompose this compound with additional fusion of the unreacted material with soda and potassium nitrite. The method suggested by Sentyurina, et al. [9] for dissolving the boron phosphide by boiling it with a mixture of HNO_3 and NaNO_3 also provides for subsequent alkaline fusion of the insoluble residue. However, the method in which the entire sample is decomposed without additional fusion is considered most suitable. Thus, the products from fusion with a mixture of alkali and sodium peroxide, or with the peroxide alone, are completely soluble in water. However, in this case, as in the others, losses are unavoidable because of the formation of phosphine [13]. If a sufficient amount of flux is used in the fusion of boron phosphide with a mixture of soda, potash and the nitrate, no ignition occurs. Samsonov and Titkov [8] used this method, taking a 80-100 fold excess of the flux. A check showed that lowering the excess flux by half also gives a complete decomposition of the sample which is soluble in hot water.

158

The phosphorus was determined using a variation of tangential complexonometric titration after precipitation of the phosphate ion by titration with a solution of bismuth nitrate using 4 ml of HNO_3 ($d = 1.4 \text{ g/cm}^3$) in 100 ml of solution. The precipitation and coagulation takes no more than 20-25 min. Then the bismuth phosphate precipitate is removed, dissolved in hot dilute HNO_3 (1 : 1) and after establishing a pH of 1.0-1.1 with NH_3 , the bismuth is titrated with Complexon III, using xylenol orange as the indicator. The phosphate ion can be precipitated with bismuth nitrate after the potentiometric determination of the boron by titration with an alkali in the presence of mannite.

TABLE 5

DETERMINATION OF PHOSPHORUS AFTER THE PRECIPITATION WITH
BISMUTH NITRATE FROM SYNTHETIC MIXTURES OF PHOSPHORUS AND
BORIC ACID (P - 18.2, B - 20 mg)

Phosphorus found, mg.		Error in the determination			
In the filtrate	In the residue	From the filtrate		From the residue	
		mg	%	mg	%
18.4	18.3	+ 0.2	1.1	+ 0.1	0.5
18.3	18.1	+ 0.1	0.5	- 0.1	0.5
18.3	18.2	+ 0.1	0.5	0.0	0.0
18.1	18.0	- 0.1	0.5	- 0.2	1.1
18.1	18.1	- 0.1	0.5	- 0.1	0.5
18.1	18.1	- 0.1	0.5	- 0.1	0.5

The results of determining phosphorus from artificial mixtures of phosphate with boric acid are given in Table 5. The composition of the boron phosphide which is obtained (on the basis of chemical analysis of several samples) is $27.1 \pm 0.05\%$ boron and $72.0 \pm 0.5\%$ phosphorus. This differs somewhat from the stoichiometric composition 1 : 1.

/59

Powders of the ternary system B-As-P were prepared by two methods. In the first, a mixture of all three components was used for the reaction in amounts which lay on the quasibinary cross section BAs - BP. In the second method, a double alloy of phosphorus with arsenic was prepared and a calculated amount of boron was added to it. After the mixtures were kept at $800-1100^{\circ}\text{C}$, depending on the composition, in ampules which had been sealed under vacuum, the phase composition was studied by x-ray diffraction method and the concentration of the main components was determined by chemical analysis. It was shown that BAs and BP form solid substitution solutions, both from the side of the boron phosphide and from the side of the boron arsenide up to 30 mole %. The homogenization of the compositions in the center section of the cross section did not result in the formation of single-phase samples.

It was noted, in the synthesis of the three component samples, that some unreacted arsenic remains; therefore, the composition of the resulting powders was determined by chemical analysis. A sample

weighing 0.15 g was fused in a platinum crucible with 5-6 g of a mixture of Na_2CO_3 , K_2CO_3 and NaNO_3 (1 : 1 : 0.25). The crucible with the mixture of the sample and the flux was placed in a muffle furnace which was switched on and brought to 750°C and kept there for 10-15 min. The button was leached with hot water and transferred to a 250 ml volumetric flask. To determine the boron, 50 ml of the solution was neutralized with hydrochloric acid to a rose color for methyl red, boiled for 5-7 min., cooled, and, after placing the glass and calomel electrodes of the LP-58 potentiometer, the pH was brought to 6.9, then the solution was titrated, after the addition of mannite, with alkali until the pH was brought to 6.9 again.

The arsenic was determined bromatometrically after distillation in a Ledebur [2] apparatus. For this, 100 ml of the solution was evaporated with sulfuric acid to remove the nitrogen oxides. The solution was transferred to the distillation apparatus and, after adding 1 g of hydrazine sulfate and 0.5 g of potassium bromide, the arsenic was distilled off in the form of the trichloride. The distillate was heated to 60°C and titrated with a bromate solution until the rose color of the methyl orange disappeared. Phosphorus was determined in the remaining portion of the solution. For this the alkaline solution was neutralized with nitric acid, using methyl red as the indicator and 4 ml more of HNO_3 ($d = 1.4 \text{ g/cm}^3$) was added per 100 ml of solution. The phosphate and arsenate were precipitated from the solution, which had been heated to boiling, by the addition of a two-fold excess of a titrated solution of $\text{Bi}(\text{NO}_3)_3$ [11]. The precipitate was filtered off through a dense filter and washed with 0.2 N *

Then the excess bismuth in the filtrate was titrated with Complexon III, bringing the pH to 1.0-1.1 with ammonia and adding xylenol orange. The phosphorus was calculated by the difference. The complexometric titration can also be done after the solution of the precipitate in warm, dilute (1 : 1) HNO_3 . The results for the precipitation of the sum of the phosphate and arsenate from synthetic mixture are given in Table 6.

*Omission in foreign text.

TABLE 6
DETERMINATION OF PHOSPHORUS IN A SYNTHETIC MIXTURE WITH ARSENIC

Taken, mmoles		Determined, mmoles		Error in determining P	
Arsenic	Phosphorus	Arsenic + Phosphorus	Arsenic + Phosphorus (tangential with Complexon)	Phosphorus (by difference)	
				mmoles	%
0.3432	0.5876	0.9308	0.9370	0.5938	+ 0.0062
0.3432	0.5876	0.9308	0.9232	0.5807	— 0.0069
0.3432	0.5876	0.9308	0.9254	0.5822	— 0.0054
0.3432	0.5876	0.9308	0.9272	0.5840	— 0.0036
0.3391	0.7103	1.0494	1.0247	0.6856	— 0.0247
0.3391	0.7103	1.0494	1.0280	0.6889	— 0.0214
0.3391	0.7103	1.0494	1.0369	0.6978	— 0.0125
					1.0
					1.2
					0.9
					0.6
					3.5
					3.0
					1.6

This method can be used to analyze the powders having a ternary composition with good accuracy.

CONCLUSIONS

1. Methods of chemical analysis are suggested for the compounds of boron with arsenic and phosphorus.

2. The formula B_6As is assigned to the hexaboride of arsenic on the basis of the chemical analysis.

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The most promising method for the analysis of alloys which contain molybdenum is complexonometry, which allows the alloys to be analyzed without the preliminary separation of the components.

A method is described in the literature for the complexonometric determination of molybdenum which is based on the formation of a complex of hexavalent molybdenum. Molybdenum (VI) forms a compound with Complexon III having a molar Mo: Complexon III ratio of 2 : 1 at a pH of 2-7 [1]. Pyrocatechol is used as the indicator in such a titration in the presence of indigo carmine as the internal light filter and a pH of 4-5 in the solution. Indirect methods have also been described for the determination of hexavalent molybdenum [5,12], for example, the method based on the precipitation of calcium molybdate, dissolving it and titrating the calcium solution with Complexon III in the presence murexide. More reproducible and accurate results are obtained in the complexonometric determination of molybdenum which has first been reduced to the pentavalent state.

Molybdenum (V) forms a complex compound with Complexon III whose composition corresponds to a ratio of the components of Mo:Complexon III = 2 : 1 which is stable in the acid range from 0.5 N hydrochloric acid to a pH of 10 [2]. Molybdenum is reduced with hydrazine hydrochloride with boiling of the solution. The determination of the pentavalent molybdenum is based on the titration of the excess Complexon III with a solution of zinc salts in the presence of chromogen black ET as the indicator at a pH of 10.

The complexonometric determination of molybdenum, reduced to the pentavalent state, is also possible using 1-(2-pyridyl-azo)-naphthol (PAN) as the indicator [6]. In this case the molybdenum is reduced

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with hydroxylamine sulfate and the excess Complexon III is titrated first with a solution of copper sulfate to a bright red color at a pH of 4.5-5 and then with a solution of Complexon III to a pure yellow color. Such a titration increases the accuracy of the determination.

The problem before us boils down to developing a method for the complexonometric analysis of alloys $\text{ZrB}_2\text{-MoSi}_2$, Mo-TiC , and Ti-MoC , molybdenum aluminide, and Cu-Mo alloys without separating the components.

For the complexonometric determination of aluminum, the destruction of its complex with sodium fluoride [3,5,9,11] is used, followed by the determination of the Complexon III which is released. This approach was used to analyze the molybdenum aluminide and the $\text{ZrB}_2\text{-MoSi}_2$ alloys.

The principle of this method consists of the following: the sum of the zirconium (aluminum) and molybdenum are determined, after the molybdenum has first been reduced to the pentavalent state, by titrating the Complexon III with a solution of zinc chloride in the presence of xylenol orange. Ammonium fluoride is added to the titrated solution (to break down the zirconium complexonate) or sodium fluoride is added (to break down the aluminum complexonate) and the Complexon III which is released is titrated with the same zinc chloride solution.

In analyzing the $\text{TiB}_2\text{-MoSi}_2$ alloys, the titanium is tied up with sodium fluoride. In analyzing the molybdenum-copper alloys, thiourea is used to mask the copper. The copper is determined by direct titration with Complexon III at a pH of 8 using murexide as the indicator.

ANALYSIS OF MOLYBDENUM ALUMINIDES

The sum of the aluminum and molybdenum are determined by titrating the excess of Complexon III with a solution of zinc chloride at a pH of 9 using eriochrom black T. Sodium fluoride is added to the titrated solution, which breaks down the aluminum complexonate, and the Complexon III which is released is titrated with a solution of zinc chloride.

Analytical method. A sample of the alloy weighing 0.2-0.3 g is dissolved with heating in 30 ml of sulfuric acid (1 : 4) with the addition of nitric acid. The solution is evaporated to the formation of sulfuric acid fumes. If an insoluble residue is present, it is filtered off, roasted and fused with potassium pyrosulfate. The solution is transferred to a 100 ml volumetric flask.

Determination of the sum of the molybdenum and aluminum. Ten milliliters of hydrochloric acid (1 : 1) is added to an aliquot part of the solution (10-20 ml) and a 1% solution of hydrazine hydrochloride is added and the molybdenum is reduced by boiling the solution for 3-5 min. An excess of Complexon III (0.025 M solution) is added to the reduced solution, kept for 5-10 min. and the eriochrome black T is added. The solution is neutralized with ammonia to a blue-green color and the excess Complexon III is titrated with a 0.025 M solution of zinc chloride until the solution's color changes to red. /63

Determination of aluminum. Sodium fluoride is added to the titrated solution and the solution is heated and the Complexon III, which is released, is titrated with a zinc chloride solution (color change from blue-green to red). This titration gives the amount of Complexon III which is bound with the aluminum.

The amount of Complexon III which is used for the molybdenum is determined from the difference between the first and second determination.

In the complexonometric analysis of molybdenum aluminide xylenol orange can also be used as the indicator. In this case the titration is done at a pH of 5. The data obtained for the titration of synthetic mixtures of molybdenum and aluminum are given in Table 1.

It was found, in analyzing the molybdenum aluminides, that the most accurate and reproducible results were only obtained in the case in which the aluminum concentration in the alloy did not exceed 50%. In other cases the change in the indicator at the equivalence point is not clear-cut and the data are not very reproducible or accurate (Table 2. /64

TABLE 1
COMPLEXONOMETRIC DETERMINATION OF ALUMINUM AND MOLYBDENUM IN
SYNTHETIC MIXTURES

Used, mg.		Found, mg		Relative Error, %	
Molybdenum	Aluminum	Molybdenum	Aluminum	Molybdenum	Aluminum
Indicator - eriochromeblack T					
4.70	3.05	4.90	2.93	+ 4.25	- 2.29
7.00	1.53	6.91	1.55	- 1.14	+ 1.92
10.50	2.29	10.30	2.29	- 1.90	0
17.50	5.35	17.23	5.42	- 1.54	+ 1.30
21.02	3.82	21.13	3.89	+ 0.52	+ 1.84
Indicator - xylenol orange					
8.17	3.44	8.31	3.49	+ 1.71	+ 1.45
10.04	5.05	9.80	5.05	- 2.30	0
11.67	6.11	11.80	6.11	+ 1.11	0
11.68	7.64	12.04	7.64	+ 3.36	0
12.84	5.35	13.07	5.35	+ 1.79	0
15.17	2.67	15.52	2.67	+ 2.83	0
23.35	3.82	23.67	3.77	+ 1.38	- 1.33

TABLE 2
REPRODUCIBILITY OF THE RESULTS FOR DETERMINING THE COMPONENTS
IN MOLYBDENUM ALUMINIDES

Taken, mg.		Found, mg		Mo : Al Ratio	Relative Error, %	
Mo	Al	Mo	Al			
21.02	3.82	21.13	3.89	5.5:1	+ 0.52	+ 1.84
17.50	5.35	17.23	5.42	3.2:1	- 1.54	+ 1.30
11.67	6.11	11.80	6.11	2:1	+ 1.11	0
4.70	3.05	4.90	2.98	1.5:1	+ 4.25	- 2.29
10.95	18.75	11.58	18.45	1:1.7	+ 5.75	- 1.6
13.20	26.42	14.08	26.10	1:2	+ 6.66	- 1.21
4.80	12.00	5.40	11.70	1:2.5	+ 12.5	- 2.5
6.18	23.70	6.90	23.40	1:3.8	+ 10.4	- 1.26

ANALYSIS OF $\text{ZrB}_2\text{-MoSi}_2$ ALLOYS

The zirconium in these alloys is determined by direct titration with Complexon III in a sulfuric acid medium (0.2 N solution) using xylenol orange as the indicator. The sum of zirconium and molybdenum are determined in another aliquot portion by back titration of the excess Complexon III with a solution of zinc salts using xylenol orange as the indicator. The molybdenum is first reduced with hydrazine

TABLE 3
COMPLEXONOMETRIC DETERMINATION OF MOLYBDENUM AND ZIRCONIUM
IN SYNTHETIC MIXTURES

Taken, mg		Found, mg		Relative Error of Determination	
Mo	Zr	Mo	Zr	Mo	Zr
24,0	20,0	24,2	20,17	+0,8	+0,85
12,0	20,0	12,07	20,10	+0,58	+0,5
12,0	10,0	11,90	9,95	-0,8	-0,5
18,0	15,0	18,30	14,80	+1,65	-1,33
18,0	25,0	18,32	24,73	+1,72	-1,08

hydrochloride. The zirconium and molybdenum can be determined for a single solution.

The sum of the zirconium and molybdenum (V) is determined at a pH of 5 by titration of the excess Complexon III with a solution of zinc salts using xylenol orange as the indicator. Ammonium fluoride is added to the titrated solution to break down the zirconium complexonate and the Complexon III which is released is titrated with a solution of zinc chloride with the same indicator. The molybdenum is determined from the difference between the first and second titration.

Method. A sample of the alloy weighing 0.2 g is dissolved in a platinum beaker by heating in a mixture of hydrofluoric and nitric acid and then 5-6 ml of sulfuric acid ($d = 1.84 \text{ g/cm}^3$) is added and the solution is evaporated to the evolution of sulfuric acid fumes. /65
The solution is transferred to a 100 ml volumetric flask and brought to to the mark with water.

Determination of the sum of zirconium and molybdenum. An aliquot (20 ml) is transferred to a tapered flask and 10 ml of hydrochloric acid (1 : 1) and 5 ml of a 1% solution of hydrazine hydrochloride are added to reduce the molybdenum. The mixture is boiled for 3-5 min. until the solution becomes yellow and then an excess of Complexon III is added. The solution is allowed to stand for 5-10 min. and then five drops of a 0.5% solution of xylenol orange is added. The solution is neutralized to a pH of 5 and 10-15 ml of a pH 5 buffer is added and the excess Complexon III is titrated with a zinc chloride solution.

TABLE 4
DETERMINATION OF MOLYBDENUM AND TITANIUM IN SYNTHETIC MIXTURES

Taken, mg.		Found, mg.		Relative error of determination, %	
Mo	Ti	Mo	Ti	Mo	Ti
183.0	55.0	182.00	58.0	-0.5	+5.5
172.0	60.0	173.0	63.0	+0.5	+5.0
153.0	69.0	155.0	70.0	+1.3	+1.4
133.0	78.0	132.0	79.0	+0.8	+1.3
114.0	86.0	114.0	86.0	0	0
95.0	95.0	96.0	96.0	+1.0	+1.0
76.0	105.0	73.0	103.0	-3.9	-1.9
57.0	113.0	55.0	113.0	+3.5	0
38.0	121.0	36.0	119.0	-5.3	-1.7

Determination of zirconium. Ammonium fluoride is added to the titrated solution and the mixture is heated. The Complexon III that is released is titrated with a solution of zinc. This determines the zirconium concentration. The molybdenum concentration is determined from the difference between the first and second titrations.

The zirconium can also be determined in the following way: Two hundred milliliters of 2 N water*, a few drops of the xylenol orange solution, are added to an aliquot portion (20 ml) of the solution and the mixture is titrated slowly with Complexon III until the rose color of the solution changes to yellow. The method was checked on synthetic mixtures and the results are given in Table 3.

ANALYSIS OF Mo-TiC and MoC-Ti ALLOYS

In analyzing Mo-TiC and MoC-Ti alloys, sodium fluoride is used to mask the titanium. Molybdenum (V) is determined by back titration of the excess Complexon III with a zinc chloride solution at a pH of 5 using xylenol orange as the indicator. The titanium is determined by back titration of the excess Complexon III with a zinc chloride solution at a pH of 5 using the same indicator [8]. Under the conditions for titrating the titanium, the molybdenum (VI) forms a complex compound with the hydrogen peroxide which does not react with Complexon III.

*This is obvious mistake in foreign.

Method of analysis. A sample of the alloy weighing 0.2 g is dissolved in 20 ml of sulfuric acid (1 : 4) with the addition of 1-2 ml of nitric acid. The solution is evaporated to the evolution of sulfuric acid fumes and transferred to a 100 ml volumetric flask and brought to the mark with water.

Determination of molybdenum. For reduction of the molybdenum, 10 ml of hydrochloric acid (1 : 1) is added to a 20 ml aliquot of the solution along with 5 ml of a 1% solution of hydrazine hydrochloride and then 0.2 g of dry sodium fluoride is added to tie up the titanium. The mixture is boiled for 3-5 min. and an excess of 0.025 M Complexon III is added. The mixture is allowed to stand for 5-10 min. and then 5-6 drops of a 0.5% solution of xylenol orange is added. The solution is neutralized to a pH of 5 with ammonia and then 10-15 ml of a pH 5 buffer is added and the excess Complexon III is titrated with a solution of zinc chloride until the color of the solution changes from yellow to orange.

Determination of titanium. An aliquot portion of the solution (20 ml) is used and 2-3 ml of hydrogen peroxide (30% solution) is added to it and then an excess of Complexon III (0.025 M solution). The mixture is allowed to stand for 5-10 min. and then 5 drops of a 0.5% solution of xylenol orange is added and the mixture is neutralized to a pH of 5 with ammonia. Then 10-15 ml of a pH 5 buffer solution is added and the excess Complexon III is titrated with a solution of zinc chloride until the solution's color changes from yellow to orange-rose.

/67

The method of analysis was checked on synthetic mixtures and on samples of alloy. In analyzing TiC-Mo alloys, the titanium and molybdenum were separated by precipitating the molybdenum with cupron. The data are given in Tables 4 and 5.

ANALYSIS OF MOLYBDENUM - COPPER ALLOYS

Thiourea is used to mask the copper in analyzing copper-molybdenum alloys. The copper is determined by titration with Complexon III at a pH of 8 using murexide as the indicator. The molybdenum is

TABLE 5
COMPLEXONOMETRIC DETERMINATION
OF TITANIUM IN TiC-Mo SAMPLES

Titanium found, %	
With removal of the molybdenum	Without removal of the molybdenum
28.7	28.9
24.8	24.8
15.8	15.8
6.9	7.1
4.2	4.2

determined after it is first reduced and the copper is tied up by thiourea by back titration of the excess Complexon III with a zinc chloride solution at a pH of 5 using xylenol orange as the indicator.

Method of analysis. A sample weighing 0.3 g is dissolved by heating it in 15-30 ml of nitric acid (1 : 1). Then 10 ml of sulfuric

acid (1 : 1) is added and the solution is evaporated to the evolution of sulfuric acid fumes.

The solution is transferred to a 100 ml volumetric flask. To determine the molybdenum, a 20 ml aliquot is transferred to a tapered flask, 10 ml of hydrochloric acid (1 : 1) and 5 ml of a hydrazine hydrochloride solution are added and the mixture is boiled for 3-5 min. until it becomes yellow. 0.5 g of thiourea are added to the hot solution and then an excess of Complexon III is added. The solution is allowed to stand for 5-10 min. and then it is transferred to a pH of 5 with ammonia, and 10-15 ml of a pH 5 buffer solution is added along with 8-10 drops of xylenol orange (0.5% solution) and the solution is titrated with zinc chloride until the color changes from yellow to orange-red.

/68

TABLE 6
DETERMINATION OF MOLYBDENUM AND COPPER IN ARTIFICIAL MIXTURES

Taken, mg.		Found, mg		Relative error of determination, %	
Mo	Cu	Mo	Cu	Mo	Cu
13.25	10.0	13.0	10.0	-1.88	0
15.00	12.0	15.25	12.15	+1.66	+1.25
15.00	8.00	15.50	8.00	+3.33	0
31.25	5.5	31.50	5.45	+0.8	-0.9
11.00	10.0	11.25	10.10	+2.27	+1.0
16.25	15.00	16.10	15.05	-0.92	0
16.25	8.0	16.45	7.84	+1.23	-2.00
17.50	12.80	18.00	12.48	+2.20	-2.5
18.75	8.00	19.00	8.00	+1.33	0
25.00	9.60	24.65	9.60	+1.40	0

To determine the copper, an aliquot portion of the solution (20 ml) is transferred to a tapered flask, diluted to 50-70 ml with water, and neutralized to a pH of 8 with ammonia. The solution is titrated with Complexon III using murexide as the indicator.

The method was checked using artificial mixtures and the data are given in Table 6.

CONCLUSIONS

Methods have been developed for the complexonometric analysis of molybdenum aluminides, ZrB_2 - $MoSi_2$, MoC-Ti, and TiC-Mo alloys and molybdenum-copper alloys without preliminary separation of the components.

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ANALYSIS OF THE GERMANIDES OF TITANIUM, ZIRCONIUM,
HAFNIUM AND TANTALUM

769

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Large amounts of germanium are determined by using gravimetric and volumetric methods. The gravimetric methods are based on the precipitation of germanium with various precipitants, e.g., the formation of the salts of pyrocatechologermanic acid with ophenantrolin [6], hydroxyquinoline [2], etc. The ability of germanic acid to form a complex acid with polyatomic alcohols or with monosaccharides, which can be titrated with alkali using various indicators [3,8], is used in the volumetric method.

Germanium can be separated from the majority of interfering elements by distilling off as germanium chloride [1,10] or by its extraction with organic solvents [3,9], precipitation with hydrogen sulfide, etc.

Fusion with an alkali and sodium peroxide, sintering with a mixture of calcium oxide and potassium nitrate [4], and also with calcium oxide and magnesium nitrate, are used to decompose samples which contain germanium. Dissolution in a mixture of hydrofluoride and sulfuric, hydrofluoric and phosphoric acids [7,12], etc., is also recommended.

We needed to analyze the germanides of the transition metals -- titanium, zirconium, hafnium and tantalum. No methods were found in the literature for the analysis of these germanides.

The germanides of the transition metals are stable compounds from the chemical standpoint. The titanium, zirconium and hafnium germanides dissolve in a mixture of hydrofluoric and nitric acid, and sinter with the following mixtures: barium carbonate + calcium oxide, magnesium oxide + sodium carbonate. In addition, titanium germanide dissolves completely in a 30% solution of hydrogen peroxide. The

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tantalum germanide dissolves in a mixture of potassium sulfate with sulfuric acid.

These data show that the selection of the reagents for dissolving the germanides is very limited if we take into account that in sintering, and also in fusion with an alkali or sodium peroxide in nickel or iron crucibles, foreign components are introduced into the solution.

Analysis of the titanium, zirconium, hafnium germanides. The method of dissolution in a mixture of hydrochloric and nitric acids and evaporation with sulfuric acid to the point of evolution of the acid fumes was used for the decomposition of the germanides.

The titanium, zirconium and hafnium were determined complexonometrically (back titration of the excess Complexon III). We know [5] /70 that prolonged heating is required for the complexonometric determination of germanium. Our experiments showed that germanium does not actually react with the Complexon III in the cold for the conditions in determining the titanium, zirconium and hafnium and, therefore, it does not interfere in their determination.

The titrometric method was used to determine germanium, i.e., the titration of the complex mannitegermanic acid with an alkali. First it was necessary to study methods for eliminating the interference from the cations (titanium, zirconium and hafnium). Their removal with barium carbonate is not expedient because, first of all, the precipitate absorbs some amount of the germanium and, second, the method is not suitable in the presence of sulfuric acid.

In determining the germanium, we tried to use the method of masking the cation with a complexing agent and got positive results. The following were tested: tartaric acid, potassium sodium tartrate and hydrogen peroxide (the latter was only used for titanium).

We know [11] that germanium forms a complex with tartaric acid over a wide range of pH with a 1 : 1 ratio of the components which is

apparently unstable and is decomposed by mannite. Thus the mannite-germanic acid is more stable.

ANALYTICAL METHOD

A sample of the germanide weighing 0.1-0.2 g was dissolved in a mixture of hydrofluoric and nitric acid and then 20 ml of 1 : 1 sulfuric acid was added and the solution was evaporated with low heat to the formation of acid fumes. When cool the solution was transferred to a volumetric flask and diluted to the mark with water. If a white precipitate of germanic acid is formed in the evaporation, it should be filtered off, washed twice with water, and dissolved in 5-10 ml of hot 20% sodium hydroxide, and this is then added to the filtrate in the volumetric flask. The titanium germanide can also be dissolved in 30% hydrogen peroxide.

For determining titanium, 11 ml of 30% hydrogen peroxide is added to an aliquot part of the solution and an excess of a titrated solution of Complexon III is added. After 10 min. the solution is neutralized to a pH of 5 and an acetate-ammoniacal buffer solution (pH 5) is added and the excess Complexon III is titrated with a solution of zinc sulfate using xylenol orange as the indicator. The titer of the Complexon III with respect to the elements is determined from a standard solution of the appropriate metal under the same conditions as those in the experiment.

Hafnium and zirconium are determined in the same way only without the hydrogen peroxide and the 10 min. waiting period. To determine the germanium, a solution of tartaric acid is added to an aliquot part of the solution (for hafnium and zirconium) calculated on the basis of 0.02-0.03 g for 0.02 g of the germanide or two-four drops of hydrogen peroxide are added (for titanium) - also per 0.02 g of the germanide. Then the solution is neutralized with a 20% solution of sodium hydroxide using phenolphthalein as the indicator, and a drop of 1 : 4 sulfuric acid is added. The excess acid is neutralized by titration with 0.02 N alkali until the solution takes on the light-rose color for phenolphthalein. Then an excess of mannite is added and after 5 min. the mannito-germanic acid which is formed is titrated with the same alkali. The

/71

TABLE 1
DETERMINATION OF GERMANIUM IN SYNTHETIC MIXTURES

System	Metal taken, mg	Germanium taken, mg	Germanium found, mg	Relative error, %
Ge—Zr	5,60	6,90	6,74	-2,3
Ge—Zr	5,60	13,81	14,10	+2,1
Ge—Ti	3,60	12,77	12,50	-2,1
Ge—Ti	3,60	5,52	5,69	+3,0

alkali titer with respect to the germanium is established using a standard solution of germanium under the same conditions as those in the determination.

Analysis of tantalum germanide. A sample of the tantalum germanide /72 was dissolved in either a mixture of nitric and hydrofluoric acid followed by reducing the solution to acid vapors or by wet fusion with a mixture of potassium sulfate and sulfuric acid. Then the resulting solution was distilled in the presence of a large amount of hydrochloric acid (the final concentration is 6 N) and the germanium was determined in the distillate by titration of the germanomannite complex with an alkali.

TABLE 2
DETERMINATION OF GERMANIUM IN SAMPLES BY THE ADDITION METHOD

Germanide	Ge Concentration, %	Ge Taken, mg	Ge Added mg	Total Ge Concentration	Ge Found, mg	Relative error, %
ZrGe ₂	57,7	5,69	12,77	18,46	18,22	-1,2
		5,69	12,77	18,46	18,13	-1,7
		5,52	6,38	11,9	12,03	+1,5
Zr ₅ Ge ₃	32,3	5,52	6,90	12,42	12,26	-1,2
		5,52	6,90	12,42	12,77	+2,8
Ti ₅ Ge ₃	47,5	8,11	6,38	14,49	14,49	0
		8,11	6,38	14,49	14,67	+1,2
Hf ₅ Ge ₃	17,8	7,59	6,90	14,49	14,49	0
		7,59	6,90	14,49	14,16	-2,3

The tantalum was determined in the solution remaining in the distillation flask by precipitation with ammonia followed by weighing in the form of tantalum pentoxide. It is, of course, possible to analyze the tantalum germanide by extracting the germanium chloride from the solution.

The experimental results on determining germanium in synthetic mixtures and by the addition method are given in Tables 1 and 2.

CONCLUSIONS

Methods were developed for the analysis of the titanium, zirconium, hafnium, and tantalum germanides. The alkalimetric method for titrating the mannitogermanic acid was used to determine germanium. The interference from zirconium, titanium, and hafnium in the germanium determination was removed by adding tartaric acid (for hafnium and zirconium) or by hydrogen peroxide (for titanium). The titanium, zirconium and hafnium were titrated with Complexon III in the presence of germanium.

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The literature data on the chemical properties of metal germanides is very limited. The germanides of the alkali metals have been characterized most extensively. Lithium germanides are known having the following composition: Li_4Ge and Li_6Ge_2 .

They decompose in moist air to form Li_2CO_3 . LiGe is more active [1].

Hohmann and Johnson [6,9] described the properties of the potassium, sodium, rubidium, and cesium germanides. Alkali metal germanides with the following compositions have been synthesized: KGe , NaGe , RbGe , CsGe and the compounds more enriched with germanium KGe_4 , NaGe_4 , RbGe_4 and CsGe_4 . All of these are only stable in an inert dry gas atmosphere. In air they decompose to form the corresponding alkali and a brown, amorphous material -- germanium hydride $(\text{GeH})_x^1$. The latter is oxidized by various oxidizing agents (nitric acid, hydrogen peroxide, etc) to the germanium dioxide. The reaction of the compounds from the Na-Ge system with water or hydrochloric acid also results in the formation of germanium hydride. The compound formed by sodium and germanium completely dissociates when heated to 480°C in a vacuum.

Magnesium forms the germanide Mg_2Ge which has a silver-gray color. Like the germanides of the alkali metals, this compound is unstable in air and within 15 min. it decomposes forming the germanium hydride. It is also readily decomposed by water [4].

Calcium forms two compounds with germanium: GeCa (silvery-white in color) and GeCa_2 . Both are unstable in air and decompose with the formation of Ca(OH)_2 or CaCO_3 and an orange powder [7,8].

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¹Data have not been given on the chemical properties of the rare earth germanides.

which is apparently the germanohydride.

The copper germanides Cu_3Ge and Cu_5Ge are very stable to the action of hydrochloric and sulfuric acids. Alloys of copper containing more than 25% germanium decompose only in aqua regia [3]. For lower concentrations of germanium, they decompose in nitric acid.

Among the germanides of the titanium subgroup, only the chemical properties of the thorium germanides have been described. Thorium forms ThGe_3 and α - and β -modifications of ThGe_2 with germanium. These compounds react vigorously with 50% hydrochloric acid, concentrated hydrofluoric acid, aqua regia, and a 10% solution of sodium hydroxide /74 at room temperature. They react slowly with 30% hydrogen peroxide, 3 and 18 N sulfuric acid, concentrated and 6 N nitric acid. They do not react with 85% phosphoric acid and a 0.1 N solution of potassium permanganate [2].

Only the chemical properties of the niobium germanides have been described in the literature [5] among the vanadium subgroup germanides. The niobium germanides NbGe_2 and Nb_3Ge react vigorously with fused soda and alkali, with 48% hydrofluoric acid, 30% hydrogen peroxide, and a cold solution of sodium hydroxide. Both of the germanides react with concentrated sulfuric acid with heating but do not react with aqua regia, dilute and concentrated hydrochloric and nitric acids, or with 6N sulfuric acid.

Molybdenum forms several germanides with germanium: Mo_3Ge , Mo_3Ge_2 , Mo_2Ge_3 and MoGe_2 . They all react with alkalis, are dissolved by hydrogen peroxide, in aqua regia, and in a mixture of nitric and hydrofluoric acids /75 [11]. The germanides Mo_2Ge_3 and MoGe_2 decompose in nitric acid or in hydrogen peroxide, forming a precipitate of germanium dioxide GeO_2 .

The iron germanides FeGe_2 and Fe_2Ge are known. An increase in the germanium concentration in the Fe-Ge system increases the corrosion resistance in air. In air, FeGe_2 does not change at all.

The chemical properties have been studied for the compounds of

TABLE 1

CHEMICAL STABILITY OF TITANIUM, HAFNIUM, AND ZIRCONIUM GERMANIDES

Solvent	Insoluble residue, %		
	Ti ₅ Ge ₃	Hf ₅ Ge ₃	Zr ₅ Ge ₃
Hydrochloric acid (concentrated)	19	21	17
Hydrochloric acid (1:1)	20	15	15
Nitric acid (concentrated)	-	84	-
Nitric acid (1:1) ¹	-	88	79
Sulfuric acid (concentrated)	19	10	12
Sulfuric acid (1:4)	37	66	54
Nitric acid = hydrochloric acid (1:3)	1	9	9
Nitric acid <u>x</u> + hydrochloric acid	0	0	0
Hydrochloric acid + hydrogen peroxide	17	17	13
Hydrogen peroxide (30%)	0	99.5	-
Bromine water	99.5	100.0	-
Sulfuric acid (1:4) + 25% ammonium persulfate	12	73	-

¹The major part of the Ti₅Ge₃ decomposes, forming a hydrolytic precipitate.

germanium with manganese: Mn₃Ge₂, Mn₅Ge₃, and Mn₅Ge₂. Systems with manganese which are rich in germanium are not acid and alkali resistant [1].

The chemical stability of rhenium germanide has been studied in the cold (from 15 min. to 24 hrs.) and for boiling (for 5 min.) [10]. The experiments showed that the rhenium germanide is very resistant to the action of various chemical reagents. Thus, it does not decompose in concentrated hydrochloric acid, in cold, dilute or concentrated sulfuric acid, in concentrated and dilute nitric acid, 85% phosphoric acid, 68% perchloric acid, 0.1 N potassium permanganate, 30% hydrogen peroxide, or with fused soda and alkali. This germanide only decomposes in hot, concentrated sulfuric acid and sodium hydroxide.

As we can see from the foregoing, the chemical properties of

TABLE 2
CHEMICAL STABILITY OF TANTALUM GERMANIDE

Solvent	Insoluble residue, %	Solvent	Insoluble residue, %
Hydrochloric acid (concentrated)	97.0	Nitric acid	98.0
Hydrochloric acid (1:1)	98.0	Sulfuric acid + potassium sulfate	0
Sulfuric acid (concentrated)	70.0	Sodium hydroxide (1%)	88.0
Sulfuric acid (1:1)	99.0	Phosphoric acid	99.0
Nitric acid (concentrated)	100.0	Bromine water	98.0
Nitric acid + hydrochloric acid (1:3)	98.0	Ammonia + hydrogen peroxide	97.0
Nitric acid + hydrofluoric acid	0	Ammonium fluoride + hydrogen peroxide	53.0
Hydrochloric acid + hydrogen peroxide	99.0	Sodium hydroxide + hydrogen peroxide	54.0
Hydrogen peroxide (30%)	97.0	Ammonium fluoride + ammonium persulfate	37.0

many germanides have not been studied, the solubility of the germanides of titanium, zirconium, hafnium, tantalum, chromium and molybdenum were studied in certain solvents. Samples of the germanides weighing 0.1 g were placed in 100 ml beakers and various solvents and their mixtures were added. The beakers were covered with water glasses and the mixtures were boiled for 1 hr. Several additions of volatile or unstable solvents were added to maintain a fixed volume and concentration for the solution. After cooling, the insoluble residue was filtered off in a No. 4 Schott crucible and weighed.

As we can see from Table 1, all of the germanides of the titanium subgroup, Ti_5Ge_3 , Hf_5Ge_3 , and Zr_5Ge_3 decompose completely in a mixture of hydrofluoric and nitric acids, and they are dissolved extensively by concentrated and dilute sulfuric and hydrochloric acids, and almost completely dissolved by aqua regia.

Ti_5Ge_3 dissolves completely in 30% hydrogen peroxide and partially in nitric acid, forming a hydrolytic precipitate.

Tantalum germanide Ta_5Ge_3 is quite stable with respect to

C-2
TABLE 3

CHEMICAL STABILITY OF THE CHROMIUM AND MOLYBDENUM GERMANIDES

Solvent	Insoluble residue, %			
	Cr_3Ge	MoGe_2	Mo_3Ge	Mo_2Ge_3
Sulfuric acid (concentrated)	47 ¹	-	-	-
Sulfuric acid (1:4)	99	-	-	-
Sulfuric acid (1:1)	51	-	74	-
Hydrochloric acid (concentrated)	0	96	97	97
Hydrochloric acid (1:1)	-	100	98	97
Nitric acid (1:1)	-	0	0	0
Phosphoric acid	-	-	100	98
Acetic acid	-	53	98	93
Hydrochloric acid + nitric acid (3:1)	15	0	0	0
Sulfuric acid + hydrochloric acid	6	-	-	-
Hydrogen peroxide	-	-	100	0
Ammonia + hydrogen peroxide	-	-	25	39
Hydrochloric acid + hydrogen peroxide	0	5	20	12
Sulfuric acid + hydrofluoric acid	0	-	-	-
Bromine water	-	29	19	21
Hydrochloric acid + ammonium persulfate	-	40	-	35
Sodium hydroxide (20%)	-	-	99	-
Sodium hydroxide + bromine water	74	-	-	-

¹Salts are formed

ordinary chemical reagents (Table 2). It does not dissolve in hydrochloric or sulfuric acids, or in aqua regia, and it only dissolves completely for wet fusion in a mixture of potassium sulfate and sulfuric acids or in mixtures of nitric and hydrofluoric acids. It dissolves to a significant extent in mixtures of sodium hydroxide with hydrogen peroxide, hydrogen peroxide and ammonium fluoride, and ammonium fluoride and ammonium persulfate.

The results of studying the solubility for the chromium and molybdenum germanides are given in Table 3. We can see from the results that chromium germanide Cr_3Ge is unstable in ordinary acids. It

dissolves in hydrochloric and sulfuric acids, in mixtures of sulfuric and hydrofluoric acids and, to a significant extent, in concentrated sulfuric acid, simultaneously forming basic salts. It dissolves almost completely in a mixture of potassium sulfate and sulfuric acid, but it also forms basic salts in this case. Nitric acid and mixtures of nitric with other acids (for example, with sulfuric) do not dissolve chromium germanide because of the passivation of the chromium.

The results of studying the solubility of the germanides in acids confirms, in general, the literature data. It should only be noted that the formation of a germanium dioxide precipitate was not observed for the dissolution of Mo_2Ge_3 and MoGe_2 in nitric acid and hydrogen peroxide.

The MoGe_2 germanide dissolves partially in acetic acid. All of the molybdenum germanides are dissolved extensively in bromine water and MoGe_2 and Mo_2Ge_3 dissolve in a mixture of sulfuric acid with ammonium persulfate.

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The studies of the selenides of the rare earth metals (REM) is mainly aimed at determining their physical properties. There are no methods in the chemical literature for chemical analysis and authors refer to data from x-ray structural and x-ray phase analyses.

A preliminary study of the chemical properties of the selenides of the rare earth metals allowed us to develop methods for chemical analysis. By studying the solubility of the REM selenides, it was concluded that it was reasonable to determine the total selenium and metal concentration in a nitric acid solution. The nitric acid completely dissolves the REM selenides with the formation of selenious acid and the metal nitrates. The determination of selenium in selenious acid presents no difficulties. Methods are described in the literature [2] for the determination of selenium which is present in solution in the form of SeO_3^{2-} .

In developing a method for determining free selenium, the solubility of the selenides was studied in water and then the reaction was used for the formation of selenosulfate from the reaction of selenium and sodium sulfite: $\text{Na}_2\text{SO}_3 + \text{Se} \rightleftharpoons \text{Na}_2\text{SeSO}_3$. Its constant $K = \frac{[\text{Na}_2\text{SeSO}_3]}{[\text{Na}_2\text{SO}_3]}$ depends on temperature [1]. As the temperature is increased, the reaction shifts towards the formation of the selenosulfate. It is stable in slightly alkaline or in neutral media in the presence of an excess of sulfite which shifts the equilibrium to the left:



The removal of the sulfite from the solution with formaldehyde or by acidifying the solution gives the quantitative separation of the red modification of selenium:

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In an acid medium, bromine oxidizes the selenosulfate to selenious acid and the sulfate. The latter does not interfere with the determination of selenium. The analytical method was checked by the method of additions (Table). The relative error in the determination is about 2%.

Thus, the total, and free selenium and the rare earth metal are determined in the REM selenides by methods of chemical analysis, gravimetric and volumetric.

TABLE

CHECKING THE CONCENTRATION OF FREE SELENIUM IN CERIUM SELENIDE BY THE METHOD OF ADDITION

Weight of Ce_2Se_3 , mg	Se_{free} Concentration, mg	Se Added mg	Se Present mg	Se Found mg	Relative error, %
110	0.44	15	15.44	15.65	+1.35
115	0.46	22	22.46	22.81	+1.56
112	0.44	17	17.44	17.67	+1.30
105	0.42	14	14.42	14.67	+1.75
108	0.43	16	16.43	16.25	-1.10

To determine the total concentration of selenium, the selenides are decomposed with nitric acid which oxidizes all of the selenium, both the bound and free selenium, to selenious acid. Since the reaction takes place vigorously, the experiment is carried out in a tapered flask with air refluxing to avoid loss of the selenium during solution. In the gravimetric method, the selenious acid is reduced with sulfur dioxide to the elemental selenium. In the volumetric method, the selenious acid is reacted with potassium iodide and the evolved iodine is titrated with sodium thiosulfate using starch as the indicator. The starch solution must be added before the iodide to avoid complicating the titration by the red amorphous selenium which is formed and which absorbs the iodine. The change in the color from blue to orange is sharp in the resulting colloidal solution of selenium.

In determining the free selenium, a sample of the selenide is heated with 2 N sodium sulfate in a flask with a condenser on a boiling water bath for 40 min. The selenium in the filtrate is determined either gravimetrically or volumetrically.

The gravimetric method is based on the decomposition of the selenosulfate with the formation of elemental selenium. Formalin is added to the solution and the selenium is formed quantitatively with the removal of the excess sulfite by the formaldehyde.

The volumetric method is based on the oxidation of the selenosulfate to give selenious acid with bromine water. The excess bromine is removed by boiling slightly, followed by the addition of a few drops of an alcoholic solution of acetanilide. The selenium in the selenious acid is determined by the method given above.

The determination of the REM in the selenides is based on their decomposition with nitric acid followed by titrating the solution with Complexon III. The lanthanoid ion forms a stable complex with Complexon III. Selenious acid, which is present in the solution, does not interfere with the determination. An aliquot part of the solution is neutralized to a pH of 4.5 with ammonia and an acetate buffer solution and a mixed indicator of alizarine C and methyl blue are added to the solution. The mixture is titrated with Complexon III while boiling until the color changes from raspberry red to dirty-green.

Controlling the concentration of Fe, Ca, and Cu in the selenides is of special interest, since the starting materials, the REM oxides, contain these impurities. In some studies, it was shown that iron selenide sublimes above 900°C . The iron in the oxides is determined according to GOST (State Standards) and a method was developed for determining the iron in the selenides which is based on the colorimetric determination of trivalent iron using sulfosalicylic acid, or on the colorimetric determination of divalent iron by the o-phenanthroline method. The trivalent iron can be reduced to the divalent with hydroxylamine hydrochloride or with sulfur dioxide, i.e., the same solution can be used which is used to determine the selenium by the gravi-

metric method.

The analytical results showed that in the selenides, which are prepared at 1100°C , the iron concentration was cut in half as compared with its concentration in the oxides and at 800°C it remains about the same. This confirms the assumption that compounds can be produced which have a lower amount of impurities than the starting materials in high temperature syntheses.

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COMPLEXOMETRIC ANALYSIS OF ALLOYS OF THE RARE EARTH OXIDES
WITH THE GROUP II OXIDES AND CHROMIUM OXIDE

/80

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One of the main problems confronting chemists is the creation of new materials which are to be used at high temperatures. The rare earth oxides (RE) (yttrium and scandium), as well as the compounds and solid solutions which they form with refractory oxides of the Group II elements, are of great interest in this respect since these compounds have very high fusion temperatures (about 2000°C) and other valuable properties.

/81

The nature of the reaction of the RE oxides, yttrium and scandium, with the refractory oxides of the Group II elements (magnesium oxide, calcium, strontium, and barium oxides) have hardly been studied at all. Therefore, such studies are of practical and theoretical interest in creating highly refractory materials based on them, for the production of special glasses, and electroceramics. The alloys of the REE (rare earth elements) with chromium oxide have interesting and important properties.

The methods which can be used to make certain determinations quite accurately and with the least loss of time are very important in the analysis of a large number of samples. Among these are complexometric titration which has been widely used in laboratory practice.

In determining and separating the REE from other elements, the gravimetric, oxalate method was used most often until recently. However, it is not suitable for production work because of the considerable expenditure of time and the low accuracy.

The volumetric, complexometric method is the most reasonable.

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Several complexometric methods, both direct and reverse, are described in the literature for determining the REE which form quite stable complex compounds with Complexon III.

A method [4] is recommended for the determination of the REE of the yttrium subgroup based on titration with Complexon III in a slightly acid medium and using a mixed indicator (a mixture of the ammonium salt of alizarinsulfonic acid and methyl blue). A method is also known for the titration of the rare earth elements using Eriochrome black T as the indicator [5]. Urotropine (pH 5) is used to establish a given acidity. It is recommended that xylenol orange [8] or arsenazo [7] be used as the indicator for the complexometric titration of the REE. It is recommended that the titration with arsenazo be carried out at a pH of 5.5 - 6.5 in the presence of pyridine.

Several variations have been suggested for the method of back titration for determining the REE; for example, titration of the excess Complexon III with a solution of zinc chloride or sulfate using Eriochrome black T as the indicator [6].

S. P. Onosov [2] suggested a method for back titrating the excess Complexon III with solution of nickel chloride at a pH of 10 in the presence of murexide. Prshibil [9] suggested a method for back titrating the excess Complexon III with lead nitrate at a pH of 5.5 using xylenol orange as the indicator.

The ability of the REE scandium and yttrium to form complexes at a pH of 3-7 and at a pH of 10 for magnesium and calcium [1] was used to develop a method of complexometric analysis for the oxide alloys of the REE, scandium and yttrium, with the alkaline earth elements.

According to this method of analysis, the concentration of the rare earth elements was determined by direct complexometric titration at a pH of 5 with pyridine and arsenazo as the indicator. The solution changes its color from violet to orange. The alkaline earth element and magnesium, which form violet colored complexes [3], are determined in this same solution by direct titration. At the equivalence

point the solution changes its color from violet to orange for titration with Complexon III. The suggested method was tested on synthetic mixtures (Table 1).

On this basis the following method is suggested for determining the rare earth and alkaline earth elements for alloys R_2O_3 (SrO, BaO, CaO, MgO). A sample, which had first been heated to a constant weight at $1000^{\circ}C$, weighing 0.2 g, is dissolved in 4 ml of hydrochloric acid (1:1). For samples of the REE with magnesium and calcium, the sample can be dissolved in sulfuric acid (1:4) with heating (if the sample does not dissolve the mixture is evaporated until acid fumes are formed). The solution is cooled, diluted with water, and transferred into a 100 ml volumetric flask. An aliquot part of the solution (25 ml) is transferred into a tapered flask and 5-6 drops of 0.5% arsenazo solution are added along with 15-20 drops of pyridine. The solution is neutralized to a pH of 5-6 with ammonia using universal indicator paper, and the solution is titrated with a 0.025 M solution of Complexon III up to the point for which the violet color becomes orange. The concentration of the alkaline earth element is determined in the same aliquot. For this, ammonia is added to the titrated solution to reach a pH of 10. In this case the color reverts to its initial color. The titration is carried out with the same solution of Complexon III until the violet color changes to orange. The titer for the Complexon III solution is determined from a standard solution of these elements under the conditions for the analysis.

/83

A number of samples were analyzed by this method. For comparison, the REE, yttrium, scandium, and the alkaline earth element were determined in the same samples by the classical gravimetric method: ytterbium and yttrium by the oxalate method, barium, calcium and strontium by the sulfate method (Table 2).

/84

As we can see from the results, the suggested method for the analysis of such alloys is quite satisfactory both in terms of the accuracy and reproducibility.

In analyzing the alloys of the REE with chromium oxide, the decomposition of the sample presented difficulties. It was suggested

TABLE 1

COMPLEXOMETRIC DETERMINATION OF THE RARE EARTH AND ALKALINE EARTH ELEMENTS
IN SYNTHETIC MIXTURES

Ytterbium Oxide - SrO						Yb ₂ O ₃ - BaO						Y ₂ O ₃ - CaO					
Ytterbium			Strontium			Ytterbium			Barium			Yttrium			Calcium		
Taken, mg	Found, mg	Relative error, %	Taken, mg	Found, mg	Relative error, %	Taken, mg	Found, mg	Relative error, %	Taken, mg	Found, mg	Relative error, %	Taken, mg	Found, mg	Relative error, %	Taken, mg	Found, mg	Relative error, %
15.23	15.23	0	18.48	18.61	+0.72	21.76	21.76	0	13.75	13.84	+0.67	40.1	40.5	+1.0	76.8	76.5	-0.42
20.4	20.4	0	16.63	16.63	0	4.8	41.07	+0.67	20.17	20.17	0	46.1	46.3	+0.44	65.4	65.1	-0.15
10.88	11.1	+1.2	13.2	13.2	0	17.68	17.54	-0.76	12.84	13.02	+1.4	80.2	80.6	+0.5	98.1	99.7	+1.67
10.88	11.01	+1.2	10.56	10.56	0	10.88	10.88	0	13.66	13.73	+1.0	60.2	60.6	+0.67	65.4	64.9	-0.75
54.4	54.4	0	27.72	27.72	0	40.8	40.93	+0.33	27.2	27.2	0	122.3	122.3	0	32.4	32.7	+1.0
38.08	38.08	0	44.88	45.14	+0.6	48.96	49.23	+0.56	38.08	37.8	-0.71	75.0	75.0	0	50.6	50.6	0
29.92	30.19	+0.9	28.51	28.38	-0.46	54.4	54.4	0	44.88	44.88	0	46.1	46.1	0	32.7	32.7	0
48.96	49.23	+0.55	62.04	62.17	+0.2	108.8	108.8	0	68.00	68.00	0	69.8	70.2	+0.57	58.8	58.8	0

Y ₂ O ₃ - SrO						Y ₂ O ₃ - BaO					
Yttrium			Strontium			Yttrium			Barium		
Taken, mg	Found, mg	Relative error, %	Taken, mg	Found, mg	Relative error, %	Taken, mg	Found, mg	Relative error, %	Taken, mg	Found, mg	Relative error, %
60.1	60.9	+1.3	26.3	25.9	-2.0	60.2	60.5	+0.67	18.3	18.1	-1.0
80.2	80.2	0	39.5	39.5	0	40.1	40.1	0	21.9	21.8	-0.83
80.2	80.2	0	7.9	8.0	+0.17	80.2	80.8	+0.75	14.6	14.4	-1.25
46.5	46.1	-0.86	26.4	26.6	+1.0	70.2	70.5	+0.57	21.0	20.9	-0.87
56.1	56.1	0	47.5	47.5	0	41.7	42.1	+0.96	36.6	36.4	-0.5
46.1	46.1	0	38.0	38.2	+0.7	56.9	56.9	0	11.3	11.4	+0.8
66.1	65.8	-0.6	52.7	52.9	+0.25	98.2	98.2	0	18.3	18.3	0
160.4	160.4	0	40.9	40.9	0	200.5	200.5	0	36.6	36.7	+0.25

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TABLE 2
DETERMINATION OF THE RARE EARTH AND ALKALI METAL ELEMENTS
(weight %) BY THE GRAVIMETRIC AND COMPLEXOMETRIC METHOD

Sample	Rare Earth Elements		Alkaline Earth Elements	
	Gravimetric Method	Complexometric Method	Gravimetric Method	Complexometric Method
Y ₂ O ₃ — SrO	67,15	67,01	32,8	32,76
Yb ₂ O ₃ — SrO	77,85	77,8	21,9	21,9
Y ₂ O ₃ — BaO	57,5	57,5	42,6	42,5
Yb ₂ O ₃ — BaO	70,45	70,4	29,55	29,5
Y ₂ O ₃ — CaO	76,83	76,7	23,2	23,1
Y ₂ O ₃ — CuO	10,05	9,9	89,9	89,8
Y ₂ O ₃ — CuO	99,2	99,1	0,7	0,7
Y ₂ O ₃ — CaO	6,4	6,3	93,5	93,6
Yb ₂ O ₃ — MgO	74,0	74,1	25,8	25,9
Yb ₂ O ₃ — MgO	50,25	50,14	49,7	49,6
Yb ₂ O ₃ — MgO	34,9	35,0	65,0	65,0
Yb ₂ O ₃ — MgO	19,2	19,3	80,7	80,7

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that they be sintered with a mixture of soda and magnesium oxide at 1000°C in aluminum oxide crucibles to decompose them. Such crucibles are stable at high temperatures and, moreover, the small amount of aluminum which goes into solutions can be readily masked with sulfo-salicyclic acid in determining the rare earth elements.

ANALYTICAL METHOD

A sample weighing 0.2 g is sintered with a five-fold amount of a mixture of sodium carbonate and magnesium oxide (5:1) in an aluminum oxide crucible for 2-3 hrs. at 900-1000°C. The cake is leached with water in a beaker and (1:4) sulfuric acid is added drop-wise while heating until the cake is completely dissolved. The solution is transferred to a volumetric flask, first oxidizing the chromium with ammonium persulfate. /85

The chromium and the REE are determined from aliquot portions; the latter by titration with Complexon III at a pH of 5 using xylenol orange as the indicator, first typing up the aluminum with sulfosalicyclic acid. The titer for the Complexon III solution is established from a standard solution of the REE. The chromium is determined by the persulfate-silver method. The method was tested on synthetic mixtures (Tables 3 and 4).

TABLE 3

DETERMINATION OF GADOLINIUM OXIDE
IN SYNTHETIC MIXTURES IN THE PRESENCE OF HEXAVALENT CHROMIUM

Taken, mg	Found, mg	Relative error, %
92.77	92.77	0
94.63	94.15	-0.4
58.26	57.52	-1.3
38.96	38.49	-1.0
74.2	74.5	+0.5
30.8	30.6	-0.7
33.39	33.39	0
66.50	66.50	0

TABLE 4

DETERMINATION OF GADOLINIUM OXIDE
AND CHROMIUM OXIDE IN SAMPLES

Gadolinium Oxide, %		Chromium oxide, %
Gravimetric oxalate method	Complexo- metric method	
—	22.9	76.6
—	23.0	76.8
44.1	44.3	55.6
44.2	44.3	55.75
52.4	52.6	47.1
52.2	52.5	47.2
65.0	65.3	34.7
65.0	65.2	34.65
—	68.8	31.0
—	68.8	31.2
—	69.8	30.3
—	69.6	30.1

CONCLUSIONS

1. A method has been developed for the analysis of the alloys of rare earth and alkaline earth oxides based on the complexometric determination of the rare earth and alkaline earth elements in the same solution at different pH using the same indicator.

2. A method is suggested for the analysis of the alloys of the rare earth oxides with chromium oxide. Sintering with a mixture of sodium carbonate and magnesium oxide (1:5) in aluminum oxide crucibles at 900-1000°C is used to decompose these alloys.

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Cr_2C (METASTABLE) AND Cr_{23}C_6 OR Cr_7C_3
ISOLATED FROM STEELS AND ALLOYS

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The presence of the alloying elements Cr, Mo, W, V, N, etc., in steels and alloys facilitates, under certain conditions, the formation of carbide or nitride phases with widely varying composition of the Me_2C or Me_2N type with a hexagonal crystal structure. The temperature range in which these phases are stable in steels and alloys depends on their degree of alloying. These phases often exist with other carbides or nitride phases which makes the determination of their chemical composition and the analysis of the distribution of the alloying elements between the various phases difficult.

Specifically, only recently was it established that the hardening of the heat resistant steels which contain 12% Cr and which are alloyed with Mo, W, and other elements, and which are widely used, depends on the features of the segregated phases of the Me_2C type, their composition and dispersion [2,3,4]. The authors designated this phase by Me_2X . This phase can either be a chromium carbide of the Me_2C type or a carbonitride $\text{Me}(\text{C},\text{N})$. The metastable phase based on Cr_2C becomes stable when it is alloyed with Mo, W, V, or N.

N. F. Lashko [1] observed the Me_2C phase in an alloy which contained 0.2% C, 18% Cr, 8.9% W, and 58% Ni with a variable concentration of vanadium of 1-4%. In this case a phase segregates based on the carbide Cr_2C which is enriched with vanadium (up to 20%) and with tungsten (up to 40%).

The chemical composition of the phases of the Me_2C type, based on chromium, which were isolated from steels containing 12% Cr, was not determined since the Me_2C phase is isolated electrolytically along with the chromium carbides Me_{23}C_6 and Me_7C_3 .

On one hand, the Me_2C phase based on chromium is analogous in chemical properties to the carbides Mo_2C and W_2C and the nitrides Cr_2N and Nb_2N with a hexagonal structure, since they all decompose in hydrogen peroxide, but on the other hand the Me_2C based on chromium decomposes in acids like the cubic chromium carbide which is not decomposed by hydrogen peroxide.

The instability of the Me_2C phase to hydrogen peroxide was used to separate it from the cubic chromium carbide. Three steels were used. Their composition is given in Table 1. A 5% solution of hydrochloric acid in hydrolytic ethyl alcohol was used as the electrolyte for the electrolytic isolation of the phases. The current density was $0.1 - 0.2 \text{ A/cm}^2$. Along with the carbide Me_{23}C_6 , a chromium carbide of the Me_2C type with a hexagonal structure having the lattice parameters $a = 2.86 \text{ \AA}$ and $c = 4.47 \text{ \AA}$ was found in the anode deposits from Steels 1 and 2 by means of x-ray structural analysis. The isolated phases from Steel 3 corresponded to the chromium carbonitride $\text{Me}_2(\text{CN})$ and Me_{23}C_6 .

TABLE 1
CHEMICAL COMPOSITION OF THE STEELS, %

Steel No.	C	Mn	Si	Cr	Ni	W	Mo	V	Ti	B	Quenching temperature, °C
1	0.15	0.50	0.50	13.60	3.05	1.66	Her	0.20	0.043	0.005	1050 (oil)
2	0.24	0.30	0.46	12.70	1.70	1.77	1.70	0.24	Her	Her	1050 (oil)
3	0.15	0.38	0.20	14.45	4.47	Her	2.48	Asota	~0.08%		1050 (water, cold treatment (-70°) 2 hrs.)

The anode deposits were treated with alkali to remove contamination by tungstic and molybdic acids which are introduced into the deposit during electrolysis. The method for separating the phases consists of the following: the anode deposit, which has been washed to remove the alkali, is placed in a 0.5 l beaker and 100 ml of hydrogen peroxide is added and it is heated on a hotplate (on a thick asbestos sheet) for 2 hrs. adding hydrogen peroxide as it decomposes.

The cubic or trigonal chromium carbide is passivated by the hydrogen peroxide and remains in the residue. The Me_2C or $\text{Me}_2(\text{C,N})$ phases are decomposed and are in the filtrate. A chemical analysis of the filtrate and of the insoluble residue indicates the amount of

the elements present in the Me_2C phase and in the Me_{23}C_6 or Me_7C_3 carbides. The results of the differential chemical analysis are given in Table 2.

The concentration of the elements in the separated phases are /88 shown in Fig. 1 for Steel 2. We can see that the Cr, Mo, and W concentration in the Me_2C phase is higher than in the Me_{23}C_6 carbide and that the Fe concentration, conversely, is much lower in the Me_2C phase than in the Me_{23}C_6 phase.

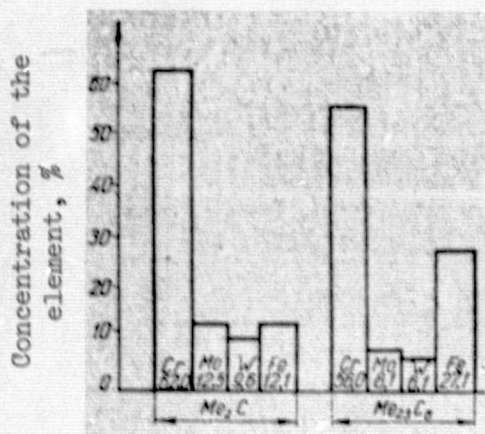


Fig. 1. Composition of the carbides Me_2C and Me_{23}C_6 for Steel 2.

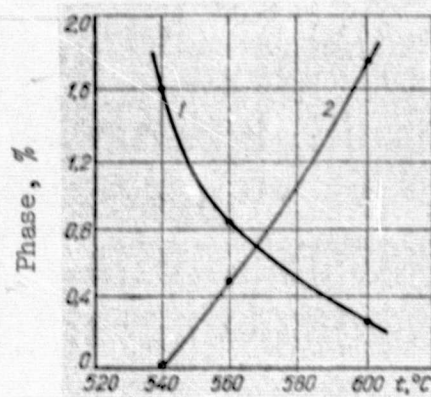


Fig. 2. The amount of the Me_2C (1) and Me_{23}C_6 (2) carbides in Steel 1 as a function of the temperature (heating time - 3 hrs)

The change in the amounts of Me_2C and Me_{23}C_6 isolated from Steel 1 is shown in Fig. 2 as a function of the heat treating conditions. After quenching from 1050°C and tempering at 540°C for 3 hrs. only a carbide of the Me_2C type based on chromium is isolated in an amount equal to 1.60%. As the tempering temperature is raised to 560°C , for the same period of time, the amount of the Me_2C carbide decreases and the cubic chromium carbide appears in an amount equal to 1.60%. With a further increase in tempering temperature to 600°C , the amount of the carbide Me_2C becomes still less and the amount of the cubic carbide is increased by approximately 3.5 times. This behavior for the Me_2C carbide can be explained by its relative stability at low temperatures and its metastability at elevated tempering temperatures. The cubic chromium carbide is the stable phase at elevated temperatures.

The kinetics for the formation of the carbides Me_2C and Me_{23}C_6 are shown in Fig. 3 as a function of the temperature of the additional heating for Steel 2. After quenching and tempering at 680°C for 4 hrs., a large amount of the chromium carbide of the Me_2C type (1.97%) and of the carbide Me_{23}C_6 (1.66%) are isolated.

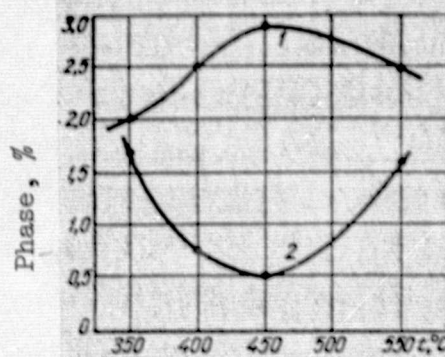


Fig. 3. Effect of the temperature for the additional heating on the kinetics for the formation of the carbides Me_2C (1) and Me_{23}C_6 (2) for Steel 2.

After additional heating at 400 and 450°C for 100 hrs., the amount of the cubic carbide decreases and the amount of the Me_2C carbide increases accordingly. As the temperature of the additional heating is increased to 550°C for the same period of time, there is a reverse change: the amount of the cubic carbide increases and the amount of the Me_2C carbide decreases accordingly. Consequently, as in the case of Steel 1, the Me_2C phase is relatively stable at lower temperatures (400, 450°C) and the Me_{23}C_6 carbide is stable at higher temperatures (550 – 650°C), and for this reason there is a redistribution of the alloying metals among the phases.

In view of the fact that nitrogen was added to Steel 3, its concentration had to be determined in the anode deposits. The addition of nitrogen to the steel makes the $\text{Me}_2(\text{C},\text{N})$ phase more stable because of the formation of chromium carbonitride which is more stable than the Me_2C type of chromium carbide.

The results of the differential chemical analysis of the anode deposits isolated from Steel 3 are given in Table 3. The value given for the carbon concentration is a calculated value. We can see from the table that during tempering at 500°C for 1 hr. a small amount of the chromium carbonitride of the $\text{Me}_2(\text{C},\text{N})$ type is formed. After a second tempering at 450 and 520°C for the same period of time, the amount of the chromium carbonitride increases. At 650°C the concentration of the $\text{Me}_2(\text{C},\text{N})$ increases to 1.75% and the amount of cubic carbide which is formed is 0.90%.

TABLE 2

RESULTS OF THE DIFFERENTIAL CHEMICAL ANALYSIS OF THE
ANODE DEPOSITS ISOLATED FROM STEELS 1 AND 2

Steel No.	Temp., °C	Time, hrs	Amt. of phase	Me ₂ X					Amt. of phase	Me ₂ /C ₂					Phase Composition
				Cr	Fe	W	Mo	V		Cr	Fe	W	Mo	V	
1	540	3	1.60	74.4	10.6	11.2	—	3.7	—	—	—	—	—	—	Me ₂ X
	560	3	0.94	73.4	12.7	11.7	—	2.1	0.54	64.8	18.5	9.3	—	7.4	Me ₂ X, Me ₂₃ C ₄
	600	3	0.31	67.7	16.1	9.6	—	6.4	1.81	64.6	21.5	12.1	—	1.7	Me ₂ X, Me ₂₃ C ₄
	680	4	1.97	60.0	11.6	10.1	14.7	3.0	1.65	58.4	22.3	7.2	9.0	3.0	Me ₂ X, Me ₂₃ C ₄
	680	4	—	—	—	—	—	—	—	—	—	—	—	—	—
2	400	100	2.47	64.0	10.9	9.3	11.9	2.6	0.65	56.7	30.0	4.6	7.6	1.0	Me ₂ X, Me ₂₃ C ₄
	480	4	2.89	62.0	13.8	9.0	11.0	2.0	0.52	53.6	33.1	6.7	7.6	1.3	Me ₂ X, Me ₂₃ C ₄
	450	100	—	—	—	—	—	—	—	—	—	—	—	—	—
	680	4	2.51	63.8	13.9	9.2	11.1	2.0	1.57	58.8	23.1	5.4	10.1	1.25	Me ₂ X, Me ₂₃ C ₄
	560	100	—	—	—	—	—	—	—	—	—	—	—	—	—

TABLE 3

RESULTS OF THE DIFFERENTIAL CHEMICAL ANALYSIS OF THE
ANODE DEPOSITS ISOLATED FROM STEEL 3

Temper- ing Temp., °C	Amt. of phase	Cr	Fe	Mo	N	C	Amt. of phase	Cr	Fe	Mo	Ni	C ¹	Phase Composition
Temp., °C													
500	0.22	72.0	9.0	9.0	2.3	7.6	—	—	—	—	—	—	Me ₂ X (C, N)
450	0.40	75.0	7.5	7.5	2.5	7.5	—	—	—	—	—	—	Me ₂ X (C, N)
520	—	—	—	—	—	—	—	—	—	—	—	—	—
650	1.74	65.5	13.8	10.9	2.3	7.4	0.88	55.7	29.5	6.8	2.2	5.1	Me ₂ X, Me ₂₃ C ₄

¹Time of tempering - 1 hr.

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It should be pointed out that the temperature range for the stability of the Me_2C phase in Steel 1 alloyed only with tungsten is narrower than that for the other two steels. After tempering at 560°C the amount of the Me_2C phase begins to decrease, and at 600°C it is only 0.31% and there is 1.81% of the cubic chromium carbide.

The Me_2C phase in Steel 2, alloyed additionally with molybdenum and vanadium, is more stable. At 550°C it is present in an amount equal to 2.51% in the presence of 1.57% of the cubic chromium carbide.

In Steel 3, which is alloyed with molybdenum and nitrogen, the phase of the $\text{Me}_2(\text{C},\text{N})$ type is even more stable. At 650°C there is more of it than of the cubic chromium carbide (1.74 and 0.88%, respectively).

CONCLUSIONS

191

1. A quantitative method is suggested for separating the carbides or carbonitrides of the type $\text{Cr}_2(\text{C},\text{N})$ and the chromium carbides M_{23}C_6 for their combined presence.

2. The concentration of iron in the Me_2X phase, based on chromium, is much less than in the cubic chromium carbide.

3. The temperature range for the existence of the metastable phase depends on the alloying of the steel. The phase is stabilized to a greater extent by molybdenum and nitrogen than by tungsten.

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CHEMICAL AND ELECTROCHEMICAL METHODS FOR THE SEPARATION
OF THE MeC CARBIDES AND Me(C,N) CARBONITRIDES
OF THE GROUP IV AND V METALS

/91

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The reactions of the MeC carbides, MeN nitrides, and Me(C,N) carbonitrides of the Group IV and V metals with mineral acids both with and without the application of a current, differ from the reactions for the carbides and nitrides of the Group VI-VIII metals. This fact can be used to isolate the individual carbides MeC and nitrides MeN from a mixture of carbides or nitrides or from steels and alloys in which these phases are present. It is more complicated to separate the MeC carbides and MeN nitrides of the Group IV and V metals from one another.

Synthetic MeC carbides of the Group IV and V metals differ from the carbides which are present in steels and alloys which have been smelted in open furnaces in their reactions with mineral acids because they also bond with nitrogen (from the materials in the charge and from from the atmosphere) and, as a rule, they contain the alloying elements (Cr, Mo, W, etc.) from the steels and alloys.

It was shown that the carbides TiC and nitrides TiN are passivated in aqueous and alcohol electrolytes which contain the Cl' , SO_4'' , PO_4''' , and NO_3' ions, and can be isolated quantitatively from various steels and alloys in contrast to the Me_{23}C_6 and Me_7C_3 carbides, which are passivated and can be isolated quantitatively only in electrolytes which contain the Cl' ion. /92

Solid solutions based on nickel are in an active state in steels and alloys and are dissolved in the electrolytes which contain the NO_3' , SO_4'' , and PO_4''' ions at potentials at which the TiC carbide and the strengthening phase $\text{Ni}_3(\text{Al},\text{Ti})$ are in a passive state. This allows the $\text{Ni}_3(\text{Al},\text{Ti})$ phase to be isolated quantitatively along with the TiC carbide or the $\text{Ti}(\text{C},\text{N})$ carbonitride.

TABLE 1

SOLUBILITY OF THE MeC CARBIDES OF THE GROUP IV AND V METALS IN STRONG ACIDS, THEIR MIXTURES, AND IN THE PRESENCE OF OXIDIZING AGENTS (for boiling).

Type of Carbide	HCl	H ₂ SO ₄	HNO ₃	HCl + HNO ₃	H ₂ SO ₄ + HNO ₃	HCl + H ₂ O ₂	H ₂ SO ₄ + H ₂ O ₂	HF	HF + HNO ₃
TiC	н	н	сл. р	р	р	р	р	—	р
ZrC	н	н	сл. р	р	р	р	р	—	р
HfC	н	н	сл. р	р	р	—	—	—	р
VC	н	н	р	р	р	р	р	н	р
NbC	н	н	н	сл. р	н	р	р	н	р
TaC	н	н	н	р	р	—	—	—	р

Remarks: According to Blanter's data [2], NbC dissolves in H₂SO₄. Here and in Table 2, H - does not dissolve; p - dissolves; сл. р - dissolves slightly.

TABLE 2

SOLUBILITY OF THE GROUP IV AND V METALS IN MINERAL ACIDS AND THEIR MIXTURES¹

Metal	HCl	H ₂ SO ₄	HNO ₃	HCl + HNO ₃	HF	HF + HNO ₃
Ti	р	р	р	р	р	р
Zr	н	н	н	р	р	—
Hf	н	н	н	р	р	—
V	н	н	р	р	р	р
Nb	н	н	н	н	н	р
Ta	н	н	н	н	н	р

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¹V. V. Nekrasov. Kurs obshchei khimii (Course in General Chemistry), Goskhimizdat, M., 1963.

The separation of the particles of the Ni₃(Al,Ti) phase from the TiC or Ti(C,N) is possible because of the ability of the Ni₃(Al,Ti) phase to be dissolved when boiled in dilute aqueous solutions of hydrochloric or sulfuric acid. The TiC carbides, Ti(C,N) carbonitrides, and TiN nitrides are not dissolved.

Finding the conditions for the chemical separation of the Ni₃(Al,Ti) phase from the MeC or Me(C,N) phase is of practical interest. The carbide (MeC) and carbonitride (Me(C,N)) phases containing three

elements - Ti, Nb, and V - are encountered most often in steels and alloys.

The results of our experiments on the chemical separation of the MeC carbides by boiling in mineral acids are given in Table 1 along with literature data [1,2]. The MeC carbides are more stable, in terms of their solubility in mineral acids, than the metals in them (Table 2).

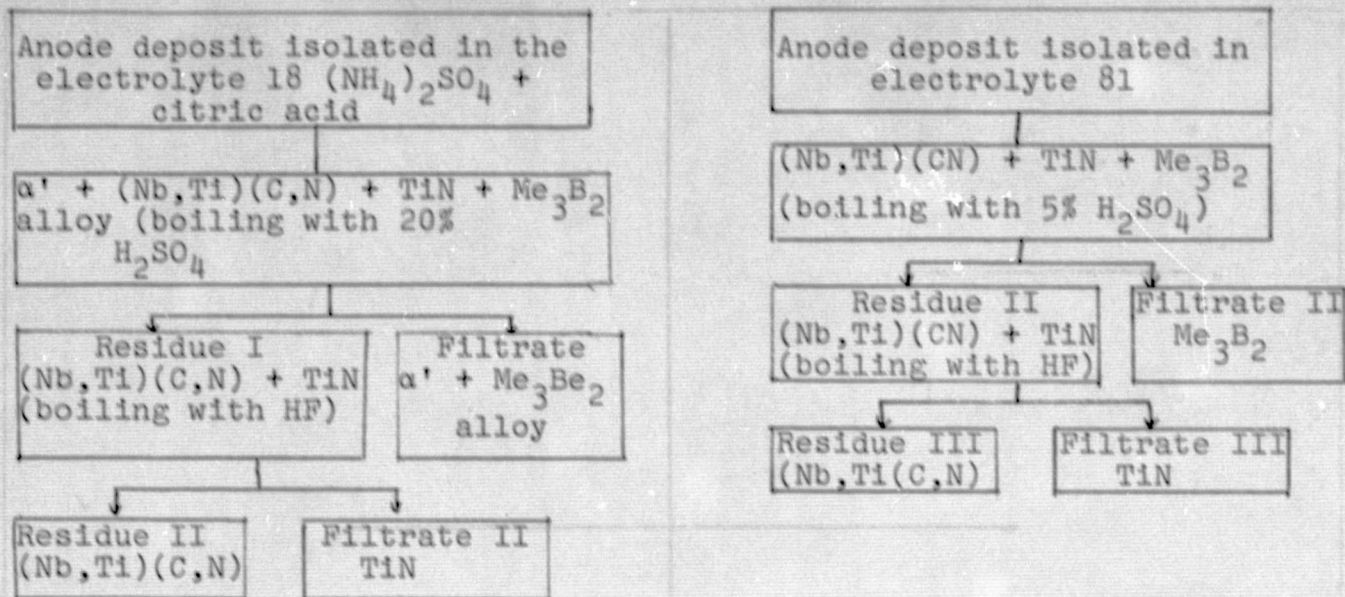
The carbides of the Group IV and V metals in the fourth period (Ti and V) have the greatest solubility. The solubility decreases for the bound metals in periods VI and V. We know that the addition of an oxidizing agent, particularly strong oxidizing agents (HNO_3 and H_2O_2) facilitates the solubility of the carbides MeC.

Judging from the data in Table 1, the chemical separation of the NbC and VC carbides should not be difficult. In studying the phase composition of a number of austenite steels, which contain niobium and vanadium (particularly El481 steel), it was shown that the carbonitride Nb(C,N) and carbide VC which are formed in them are separated by boiling in nitric acid ($d = 1.4 \text{ g/cm}^3$) [4]. The vanadium carbide dissolves in this case.

A special study was made of the separation of the phases $\text{Ni}_3(\text{Al, Ti})$, Nb(C,N), and TiN which are formed in nickel alloys of the EI-698 type. The chemical composition of these alloys is given in Table 3. The heat treatment was carried out under the following conditions: quenching from 1120°C (8 hrs.) + 1000°C (4 hrs.) + 775°C (16 hrs.) cooling in air after each operation. According to the data from x-ray structural analysis¹, the EI-698 alloy is a multiphase system in which along with the solid solution austenite, the following phases are present: $\text{Ni}_3(\text{Ti,Al})$, (Nb,Ti) (C,N), TiN, and the boride phase $(\text{Mo,Cr})_3\text{B}_2$. /94

The phases can be separated and determined individually by the following scheme:

¹K. V. Smirnov did the x-ray structural studies.



The anode deposit isolated in an aqueous electrolyte (18) which contains 10 g of ammonium sulfate, and 30 g of citric acid, which is enough to prevent the precipitation of niobic acid from the solid solution, is boiled with a 20% solution of H_2SO_4 during which the α' -phase and the Me_3B_2 boride go into solution. The concentration of the boride phase can be ignored since no more than 0.01% of the boron is present in the alloy, and the boride phase is not usually completely separated in aqueous electrolytes which contain sulfates.

The anode deposits which are isolated in the alcoholic electrolyte 81, which contains the Cl^- ion and which consists of $(Nb,Ti)(C,N)$, TiN , and Me_3B_2 (the latter is completely isolated in this electrolyte) is boiled with a 5% solution of sulfuric acid for 1.5 hrs. during which the Me_3B_2 dissolves completely.

The selective dissolution of titanium (Table 4) was observed for boiling the anode deposit which is isolated from the EI-698 alloy

TABLE 3. CHEMICAL COMPOSITION OF ALLOYS STUDIED (NITROGEN CONTENT — 0.03%)¹

C	Cr	Ti	Al	Mo	Nb
0.024	14.36	2.62	1.47	2.99	1.96
0.053	14.36	2.62	1.47	2.99	1.96
0.087	14.36	2.62	1.47	2.99	1.96
0.12	14.33	2.7	1.65	2.93	2.14
0.20	14.33	2.7	1.65	2.93	2.14
0.31	14.33	2.7	1.65	2.93	2.14

¹Phase composition of α' (Nb, Ti), (C, N), TiN , Me_3B_2

TABLE 4

SOLUBILITY OF THE ISOLATED CARBONITRIDES IN ACIDS AND THEIR MIXTURES (alloy of the EI-698 type, C = 0.31%)

Phase	Solution	Time	Residue		Filtrate	
			Nb	Ti	Nb	Ti
(Nb, Ti) (C, N) + TiN	HF (concentrated)	1.5 h	1.20	0.49	Not found	0.03
	HF (50%)	1.5 h	1.26	0.48	"	0.04
	HNO ₃ (concentrated)	3 h	1.16	0.07	"	0.45
	HNO ₃ (concentrated)	5 h	1.18	0.08	"	0.44
	50 ml H ₂ SO ₄ (1:4) + 2 ml HNO ₃	5 min	Not found		1.20	0.55
	50 ml HCl + 2 ml HNO ₃	5 min	"		1.24	0.53
	HNO ₃ + 1% NaF	5 min	"		1.22	0.54

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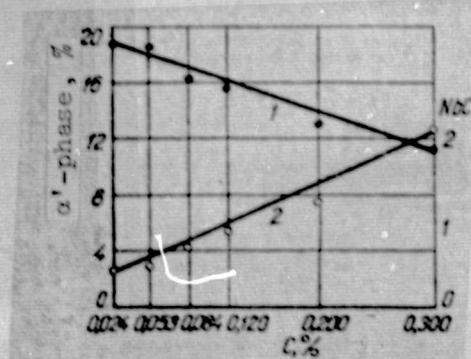
CONCENTRATION OF THE ELEMENTS IN THE
Ni₃(Ti,Al) PHASE, %

C in the Alloy, %	Ni	Ti	Cr	Mo	Nb	Al	Sum of the Elements, %
0.024	14.72	1.50	0.49	0.12	0.60	0.95	18.90
0.053	14.48	1.49	0.49	0.12	0.60	0.93	18.58
0.087	13.00	1.23	0.50	0.11	0.59	0.84	16.29
0.12	12.31	1.16	0.46	0.10	0.48	0.83	15.47
0.20	11.16	1.03	0.44	0.10	0.45	0.70	13.88
0.31	8.62	0.92	0.40	0.08	0.41	0.62	11.24

TABLE 6

CONCENTRATION OF THE ELEMENTS IN THE PHASES
(Nb,Ti)(C,N) + TiN + Me₃B₂, %

C in the Alloy, %	Ni	Nb	Ti	Cr	Mo	Sum of the Elements, %
0.024	<0.01	0.24	0.13	0.02	0.06	0.45
0.053	<0.01	0.25	0.14	0.03	0.09	0.51
0.087	<0.01	0.33	0.18	0.04	0.10	0.65
0.120	<0.01	0.52	0.22	0.04	0.11	0.89
0.20	<0.01	0.73	0.33	0.04	0.16	1.26
0.31	0.01	1.24	0.54	0.08	0.26	2.12



Dependence of the concentration of the α' -phase (1) and of the NbC(2) in the EI-698 alloy on the carbon concentration.

which contains niobium carbonitride and a small amount of titanium nitride. After boiling with nitric acid, a large amount of titanium was found in the filtrate. According to the x-ray structural analysis results, before boiling with nitric acid the elementary cell parameter of the carbonitride (Nb, Ti)(C,N) is equal to 4.393 Å and after selective dissolution of the titanium it changed to 4.397 Å.

The anode deposit which contains the (Nb,Ti)(C,N) and TiN phases dissolves completely in a mixture of hydrochloric and nitric acids and also in a mixture of sulfuric and nitric acids and in the presence of hydrogen peroxide.

The composition of the α' -phase was determined by means of the chemical separation of the phases. The concentration of the α' -phase can be determined by two methods, regardless of the carbon concentration in the alloy. The carbide and carbonitride phases of niobium and titanium are separated quantitatively in an alcoholic electrolyte which contains hydrochloric acid and also in aqueous electrolytes which contain ammonium sulfate.

The data on the concentration of the α' -phase, determined by means of the chemical separation of the phases in the anode deposits and found by differences in the results obtained by two methods for the electrochemical separation in electrolytes which contain either the Cl^- or SO_4^{2-} ions, agree within the limits of experimental error. The averaged data on the concentration of the α' -phase are given in Table 5 as a function of the carbon determined by different methods. The concentration of the α' -phase decreases from 18.9 to 11.2% as the carbon is increased from 0.02 to 0.31%. The carbonitride and nitride phases increase, in this case, from 0.45 to 2.12% (Table 6). The change in the concentration of the α' -phase and of the carbides is shown in the figure as a function of the carbon present in the alloys.

1. The Me_C carbides and $\text{Me}(\text{C},\text{N})$ carbonitrides of the Group IV and V metals can be isolated quantitatively in electrolytes which contain the Cl' , SO_4'' , NO_3' , and PO_4''' ions; therefore, the composition of the strengthening phase, based on Ni_3Al in heat resistant alloys which also contains the phases MeC or $\text{Me}(\text{C},\text{N})$, can be determined by two methods: using the chemical separation of the anode deposit isolated in an aqueous electrolyte containing the NO_3' , SO_4'' , or PO_4''' ions or by the difference between the data found with double electrolytic isolation of the two phases in an aqueous and alcoholic electrolyte (containing the Cl' ion).

2. For prolonged boiling of the carbonitride $(\text{Nb},\text{Ti})(\text{C},\text{N})$ with nitric acid (3-6 hrs.), selective dissolution of titanium occurs.

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ELECTROLYTIC SEPARATION OF THE α -PHASE FROM HEAT RESISTANT STEELS AND THE DETERMINATION OF ITS COMPOSITION

/97

E. F. Yakovleva, I. M. Dubrovina, and L. V. Stegnukhina*

The conditions for the formation of the α -phase and its effect on the properties of steels and alloys has not been definitively established as yet. Therefore, further studies in the area of developing methods for the differential electrochemical analysis of steels and alloys, which contain the α -phase and also other phase components, are of great importance. Studies were made of the austenite, boiler-turbine steel EP17 and the heat resistant steel meant for long-term service at high temperatures with the following chemical composition:

/98

	C	Si	Mn	Cr	Ni	Ti	W	Mo	Nb	B
EP17	0.08	0.30	1.72	19.2	14.3	—	2.57	—	0.93	0.005
EP508	0.08	0.50	0.5	13.0	18.0	1.3	1.3	1.3	—	0.005

According to the data of a preliminary micro structural analysis, the main phases in the EP17 steel are Nb(C,N), Fe_2W , M_{23}C_6 , and in the EP508 steel they are Ni_3Ti , $\text{Fe}_2(\text{W},\text{Mo})$ and $\text{Ti}(\text{C},\text{N})$. The α -phase was observed in the sample of EP17 aged at 700°C for 5000 hrs., and for a sample of the EP508 steel aged at 700°C for 5688 hrs. Parts made of EP17 and EP508 steels are used for long service items. Therefore, the study of the phase conversion under various types of heat treatment was of great interest. We know from the literature data that the hardnesses and tensile strength of steel increase as the α -phase is formed and the plasticity decreases. In rare cases, the α -phase can be the strengthening phase. The segregation of the α -phase along the grain boundaries is not desirable since it results in their impoverishment in chromium. This causes a tendency to intercrystallite corrosion and embrittlement.

In the literature, α -phases having different stoichiometric compositions are encountered: CrMn_3 , CrCo , FeCr . The iron in the α -phase

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may be replaced by V, Mo, W. As yet, Nb and Ta have not been observed in the α -phase. The α -phase of the FeCr type was studied. The microstructure of the EP17 steel with large segregations of the α -phase is shown in Fig. 1.

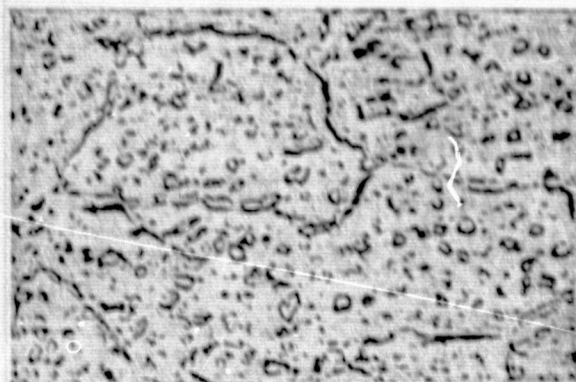


Fig. 1. Microstructure of EP17 steel with large segregations of the α -phase.

Electrolyte's Composition

1150 ml methanol and 50 ml hydrochloric acid

200 g KCl, 200 ml hydrochloric acid, 50 g ammonium citrate in 1.1 water

5 g oxalic acid and 200 ml hydrochloric acid in 1.1 of water

N. F. Lashko indicates that /99

strong carbide-forming elements (Nb, Ti, Zr) facilitate the formation of the α -phase. These elements are present in the EP17 and EP508 steels.

A number of electrolytes were tested for the isolation of the α -phase from EP17 steel:

Electrolysis Conditions

Current density 0.05 A/cm^2 , temperature 5°C , electrolysis time 1-1.5 hrs.

Current density 0.05 A/cm^2 , temperature 20°C , electrolysis time 1-1.5 hrs.

Current density 0.05 A/cm^2 , temperature 20°C , electrolysis time 1-1.5 hrs.

X-ray structural analysis¹ showed that $\text{Nb}(\text{C},\text{N})$, M_{23}C_6 , and Fe_2W were isolated from all of the electrolytes and a phase of the FeCr type was observed only in the sample which had been aged at 700°C for 5000 hrs. in place of M_{23}C_6 . This phase had a tetragonal crystal lattice with cell parameters of $a = 8.79 \text{ kX}$, $c = 4.55 \text{ kX}$.

Differential chemical analysis was done to confirm the presence of the α -phase. This was based on treating the anode deposit with an

¹V. A. Belyaeva did the x-ray structural analysis.

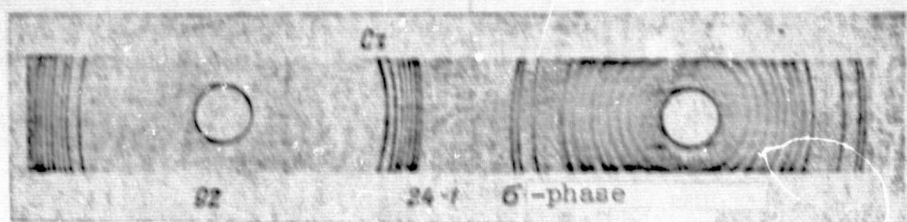


Fig. 2. X-ray diagram for the pure α -phase

equivolume mixture of 20% tartaric acid and 30% H_2O_2 . The α -phase is passivated and it remains in the residue and $Nb(C,N)$ and Fe_2W dissolve completely. The completeness of the phase separation was confirmed by x-ray structural analysis. An x-ray diagram was obtained for the pure α -phase which serves as a standard for reading the x-ray diffraction diagrams (Fig. 2).

The chemical analysis of the deposit was made after its electrolytic deposition in an electrolyte having the same composition as that used for the x-ray structural analysis. However, the results of the chemical analysis showed that the formation of the α -phase from this electrolyte is not always quantitative, since parallel analyses did not give good reproducibility. /100

The α -phase is formed most quantitatively from an electrolyte which contains hydrochloric and oxalic acid. The α -phase was formed from this electrolyte in an amount equal to 3.89 weight % and 2 weight % from the preceding electrolyte.

The concentration of the elements in the phase for sample 24-11 which was tempered at $700^\circ C$ for 5000 hrs. was:

Element	Weight, %	Atomic, %
Cr	43.96	48.22
W	7.71	2.35
Fe	48.32	49.33

In this case the atomic ratio $Fe/Cr+W = 0.97$, i.e., according to the results of the chemical analysis, it approaches the stoichio-

metric ratio which is equal to 1. In addition to the α -phase, the Nb(C,N) and the Laves phase based on Fe_2W were found in this alloy. The composition of the Nb(C,N) phase was determined after treating the anode deposit with hydrofluoric acid in which the Nb(C,N) does not dissolve. The composition of the Laves phase was calculated from the difference between the data from the chemical analysis of the total anode deposit and the sum of the niobium carbonitride and the α -phase. /101 The results of the differential chemical analysis are given in Table 1. The elements were determined as follows: Niobium - photolorimetrically with cyanoformazane; tungsten - photolorimetrically with thio-cyanate; iron - photolorimetrically with sulfosalicyclic acid; chromium by the volumetric persulfate-silver method.

TABLE 1
RESULTS OF THE DIFFERENTIAL CHEMICAL ANALYSIS OF THE PHASES ISO-
LATED FROM EP17 STEEL (Heat Treating Conditions:
700°C for 5000 hrs.)

Phase	Concentration of the elements in the phases		Concentra- tion of the phase	Atomic ratio
	Weight %	Atomic %		
(Fe, Cr) ₂ W	—	—	0.94	$\frac{\text{Fe} + \text{Cr}}{\text{W}} = 2.09$
Fe	0.13	23.50	—	—
Cr	0.23	44.66	—	—
W	0.58	31.83	—	—
Nb(C, N)	—	—	—	—
Nb	0.74	—	—	—
W	0.014	—	—	—
N ₂	0.017	—	—	—
α -phase	—	—	3.89	$\frac{\text{Fe}}{\text{Cr} + \text{W}} = 0.97$
Cr	1.71	48.30	—	—
W	0.30	2.35	—	—
Fe	1.88	49.33	—	—

An electrolyte containing 20% potassium chloride and hydro-chloric acid and 8% ammonium citrate was used to isolate the α -phase from the EP508 heat resistant steel after aging at 700°C for 5688 hrs. The electrolysis conditions were: Current density 1 A/cm², electrolyte temperature 0°C, electrolysis time 10-15 min. The x-ray structural analysis of the anode deposit showed the presence of the Laves phase

TABLE 2
RESULTS OF THE DIFFERENTIAL ANALYSIS OF THE PHASES ISOLATED FROM
EP508 STEEL (Sample 71-1)

Phase	Concentration of the Elements in the Phases		Concentration of the phase	Atomic ratio
	Weight %	Atomic %		
Ti (C,N)	—	—	—	—
Ti	0.30	—	—	—
W	—	—	—	—
Mo	0.03	—	—	—
N ₂	0.08	—	1.997	$\frac{Fe + Cr}{W + Mo} = 1.9$
Fe ₂ (W, Mo)	—	—	—	—
Fe	0.71	50.25	—	—
W	0.53	11.42	—	—
Cr	0.197	15.09	—	—
Mo	0.56	23.22	—	—
α -phase	—	—	—	$\frac{Fe}{Cr + W + Mo} = 1.2$
Fe	0.21	55.45	—	—
Cr	0.11	31.12	—	—
W	0.08	6.78	—	—
Mo	0.04	6.64	—	—

based on Fe₂(W,Mo) and Ti(C,N) in addition to the α -phase. The method developed for the EP17 steel was used for the chemical separation of the α -phase from Fe₂(W,Mo) + Ti(C,N), i.e., treatment of the anode deposit with a mixture of tartaric acid and Perhydrol in which the Laves phase and the titanium carbonitride dissolve and the α -phase remains in the residue. The cleanness of the phase separation was confirmed by x-ray structural analysis, which was done by V. A. Belyaeva and V. G. Kostogonov. The differential chemical analysis of the α -phase showed that Fe, Cr, W, and Mo are present in it. The atomic ratio of the iron to the sum Cr + W + Mo is equal to 1.2, which is close to the stoichiometric value. The results of the differential chemical analysis are given in Table 2. /102

CONCLUSIONS

1. A method was developed for the differential chemical analysis of Nb(C,N), Fe₂W, and the α -phase isolated from austenite EP17 steel and Ti(C,N), Fe₂(W,Mo) and the α -phase isolated from the heat-resistant EP508 steel.

2. On the basis of these methods, the chemical composition of the α -phase in these steels was determined.

3. The method has been adopted in laboratory practice.

REACTION OF THE REFRACTORY GROUP V METALS WITH ZINC

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Z. P. Terent'eva, and T. I. Mazina*

Because refractory compounds of the transition metals [2], particularly V, Nb and Ta, can be produced in a zinc melt, the reaction has been studied for these metals with zinc. The data which are now available on the V-Nb and Ta-Zn systems are incomplete and not precise. The most detailed and broad studies of these systems have been made by K. Shubert, et al. [7,9]. The structural characteristics of the intermetallic phases in these systems are given in Table 1. As we can see, the structures and elementary cell parameters have only been determined for a few of these compounds. The system Nb-Zn has been studied most extensively.

The reactions were studied between the refractory metal powders with an excess amount of fused zinc at the boiling point 907°C . The boiling time varied in the range of 10-30 min. The concentration of the metal in the compositions did not exceed 10% by weight. The oxidation of the surface of the boiling zinc was prevented with a stream of argon. The niobium zincide intermetallide was separated from the zinc by treating the contents of the quartz test tube, after its solidification, with $\text{HCl}(1:1)$. The intermetallide was obtained in the form of a powder. The vanadium zincide is less stable and it dissolves in the acid along with the zinc. The tantalum zincide is separated along with tantalum. /103

Since the niobium zincide is obtained in a pure form, it has been studied more thoroughly. Segregation forms are clearly visible in polished microsections: the grain boundaries are well marked, apparently being individual crystals. Their shape is hexagonal with some uneven sides. In one cross-section (Fig. 1), dendrites are seen and skeletal growth forms with inclusions of the mother melt. The Vickers hardness varies from 90 to 338 kg/cm^2 for different grains,

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TABLE 1
STRUCTURAL CHARACTERISTICS OF THE PHASES IN THE V-Nb AND Ta-Zn
SYSTEMS

Phase	Structure	Lattice Parameters Å			Literature Source
		a	b	c	
V_4Zn_8	—	8.91	—	3.22	[8]
VZn_{-3}	Cu	3.84	—	—	This work
VZn_3	Cu_3Au	—	—	—	[8]
$NbZn$	—	—	—	—	[10, 11]
Nb_2Zn_3	—	—	—	—	[2, 11]
$NbZn_2$	Ni_2Mg	5.05	—	16.32	[7]
$NbZn_{2.0-2.7}$	Cu	3.9325	—	—	This work
$NbZn_3$	Cu_3Au	3.932	—	—	[9]
		3.934	—	—	[6]
Ta_4Zn_5 ?	HF_4Zn_5	—	—	—	[3]
$TaZn_2$?	—	—	—	—	[3]

which indicates a wide range of homogeneity.

The chemical analysis of the niobium zincide [1,3] was carried out in the following way: a sample weighing 0.2 g was dissolved by heating in a mixture of concentrated acids (4 ml HF + 2 ml HNO_3) and 2-3 ml of H_2SO_4 was added. The mixture was evaporated to the evolution of SO_3 fumes and the main part of the niobium was removed by means of tartrate hydrolysis. The zinc was precipitated from the filtrate in the form of the sulfide, filtered off, roasted, and weighed as ZnO and converted to Zn. The conversion factor was 0.8034. After the hydrogen sulfide was removed, the Nb in the filtrate was precipitated with cupferron, roasted and weighed as Nb_2O_5 . The Nb_2O_5 precipitates, after separation by tartrate hydrolysis and with cupferron, were added together and converted to Nb. The conversion factor was 0.6990. /104

The method was tested on synthetic mixtures. The mean square error was ± 0.5 for Nb, and $\pm 0.4\%$ for Zn. The results of the chemical analysis showed that the composition of the compound is given by the averaged formula $NbZn_{2.35}$. A variation is observed in the Nb to Zn ratio from $NbZn_2$ to $NbZn_{2.7}$, which indicates the wide range of homogeneity for

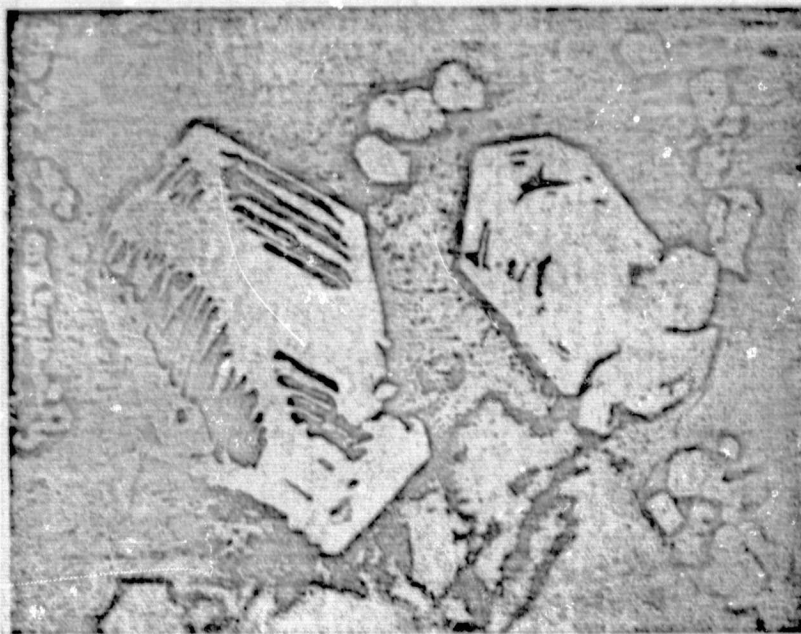


Fig. 1. Microcross section with the phase $\text{NbZn}_{2.0-2.7} \times 64$.

this intermetallide.

The results of the x-ray structural analysis of the powder led to the suggestion that the niobium zincide had a copper structure which was confirmed by calculating the intensity of the reflections on the diffraction diagram based on the assumption that the Nb and Zn atoms are set in a disordered way at the interstices of the copper lattice. The lattice period is 3.9325 \AA and the accuracy of determining the period is $\pm 0.0001 \text{ \AA}$. The interatomic distance is 2.78 \AA , which is close to the sum of the atomic radii for Nb and Zn, which is equal to 2.84 \AA . It is interesting to compare these data on the structure of $\text{Nb-Zn}_{2.0-2.7}$ with Vold's results [10/ from studying the compound NbZn_3 . Vold found a Cu_3Au type structure for it with a lattice period of 3.934 \AA . The relationship between the compound studied by Vold and by us is obvious. /105

The NbZn_2 has an ordered structure based on the structure for copper. The zinc in it occupies the positions in the center of the face. Vold studied the disordering at $470-870^\circ\text{C}$. It was not observed. Our data show that disordering takes place when the composition differs from the stoichiometric value.

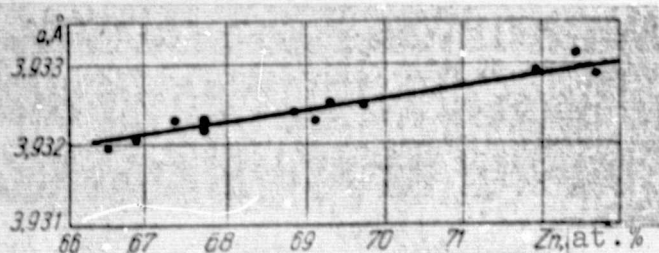


Fig. 2. Relationship between the elementary cell parameters and the zinc concentration in the compound $\text{NbZn}_{2.0-2.7}$

The changes in the lattice period were studied as a function of the change in the composition. A change in the zinc concentration within the range of 6.2 at. % corresponds to a range of fluctuation in the lattice period of 0.0009 Å. A linear increase was found in the lattice period with an increase in the zinc concentration (Fig. 2).

This dependence is explained by comparing the ionic radii of Nb and Zn and not the atomic radii as in the case of the intermetallic compounds.

From this we reach the conclusion that the metallic bond in the compound is not pure and it becomes more covalent in the presence of impurities which was confirmed by the properties of the compound, e.g. its stability. The decrease in the interatomic distance as compared with the sum of the atomic radii for Nb and Zn also indicates the stronger reaction.

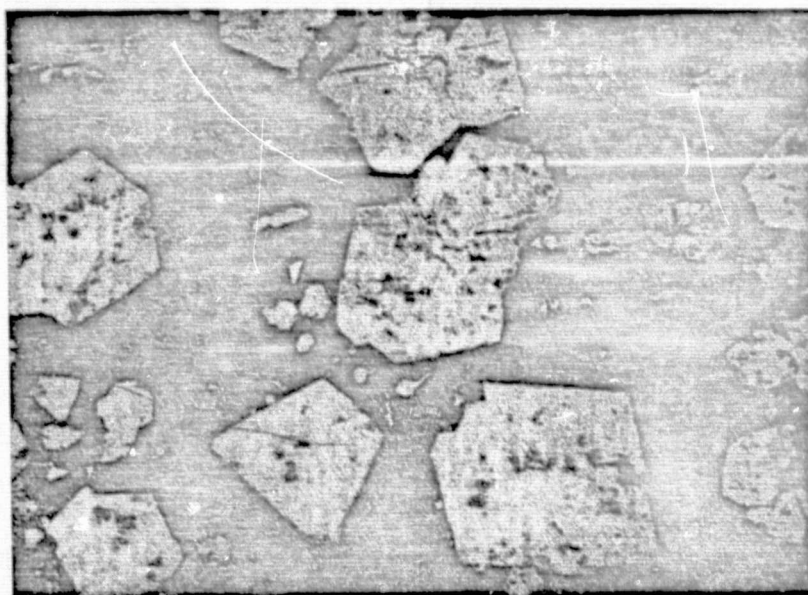
The solubility of the intermetallide was studied in dilute and concentrated alkalis and in concentrated acids, both in the cold and with heating. As we can see from Table 2, it is almost insoluble in boiling concentrated HNO_3 . It dissolves somewhat better in HCl and in alkalis and dissolves completely in boiling concentrated H_2SO_4 . An analysis of the filtrate showed that the stoichiometry is destroyed. For dissolution in acids, the Zn to Nb ratio increases, and in alkalis, particularly dilute alkalis, it decreases. The chemical individuality of each of the components of the compound is expressed in this way.

The compound of vanadium with zinc was observed in cross-sections. It could not be isolated since it dissolves in acids with the predominating dissolution of the zinc, as shown by x-ray analysis. We can see from Fig. 3 that vanadium reacts completely with zinc to form the intermetallide. The change in the microhardness from 120 to 298 kg/cm^2 indicates a wide range of homogeneity for it. The shapes of the segregations are the same in all cross-sections. These are iso-

TABLE 2
BEHAVIOR OF NbZn_{2.5-2.7} IN DIFFERENT MEDIA IN THE COLD (1 hr.)
AND WITH HEATING (2 hrs.)

Medium	In the Cold			With Heating		
	Insoluble residue, %	Concentration in solution, %		Insoluble residue, %	Concentration in solution, %	
		Nb	Zn		Nb	Zn
HCl	19.23	27.20	53.47	14.49	30.45	50.66
HNO ₃	96.96	—	—	99.20	—	—
H ₂ SO ₄	69.18	9.51	19.02	None	Initial	Initial
3HCl + HNO ₃	64.82	10.43	22.77	36.22	19.47	41.81
HF + HNO ₃	None	Initial	Initial	None	Initial	Initial
NaOH (1%)	90.08	9.28	3.28	59.56	18.86	19.67
NaOH (10%)	60.24	14.21	24.69	8.72	32.57	57.30
KOH (1%)	93.52	1.90	1.20	83.86	6.95	8.06
KOH (10%)	75.04	7.88	14.96	13.95	30.37	52.76

lated, circumscribed grains which, for the most part, have a quadrangular shape (rhombus, square), regular triangles, and hexagonals often with uneven sides. Skeletal growth forms of crystals and growths of the penetration twin type at right angles are encountered. A cubic symmetry can be assumed on the basis of the shape of the grains.



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Fig. 3. Microsection with the intermetallic phase in the V-Zn system. x 64

An x-ray study of the powder showed that the vanadium zincide has the copper structure with a cell parameter of 3.84 Å. The interatomic distance (2.72 Å) almost coincides with the sum of the atomic radii (2.73 Å). The compound VZn_3 with a cubic, Cu_3Au structure was reported by Robteutschler and Shubert [6].

By comparing the structures of $NbZn_3$ and VZn_3 and our niobium and vanadium zincides, it may be assumed that the vanadium intermetallide that was obtained has the same chemical and structural relationship with VZn_3 as the $NbZn_{2.0-2.7}$ has to $NbZn_3$ and that its structure is the result of disordering in the VZn_3 compound because of the lowering of the Zn concentration.

Since the tantalum intermetallide could not be isolated, the formation of a compound of Ta with Zn was established by measuring the microhardness of the phase present in the zinc which has a high reflecting ability. The Vickers microhardness of the intermetallide is approximately equal to 320-360 kg/cm² and that for tantalum is 165 kg/cm². /107

CONCLUSIONS

1. A new intermetallic compound was obtained for niobium with zinc having a variable composition $NbZn_{2.0-2.7}$. Its structure and elementary cell parameters were determined.
2. A compound was observed in the V-Zn system with a copper structure which has a wide range of homogeneity and the parameters of the elementary cell and the approximate composition were determined.
3. The order-disorder phenomenon was observed in the Nb-Zn and V-Zn systems.
4. A method of chemical analysis was suggested for the niobium zincide and its solubility in acids and bases was studied.

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/108

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The determination of tungsten in molybdenum is a complex analytical problem. They are separated by precipitating the molybdenum with hydrogen sulfide in the presence of tartaric acid. The tungsten is determined in the filtrate [2]. The error of the determination is large at low concentrations.

At the present time methods based on the use of organic precipitating agents are recommended for the gravimetric determination of tungsten. Chernikhov and Goryushina [9], Gusev and Kumov [4] use pyramidon for the precipitation of tungsten. Golubtsova [3] uses β -naphthoquinoline for the gravimetric determination of tungsten in steels and in ferrotungsten. Rivanol (ethodin), methylene blue, and nicotine [5] are also recommended. A method has been described for determining tungsten with hydroxyquinoline in the presence of Complexon III [7]. In the ASTM Standards for 1965, cinchonine with additions of benzoinoxime is recommended for the gravimetric determination of tungsten.

The thiocyanate method [2,6] is used for the colorimetric determination of tungsten and molybdenum. It is based on the formation of thiocyanate complexes of molybdenum and tungsten at different acidities of the solution. The dithiol method is also used [2,8,10].

Hexavalent molybdenum is extracted completely with dithiol in petroleum ether from media which are 6-14 N with respect to sulfuric acid. Tungsten forms an analogous complex with the dithiol only in a medium which is 0.5-2 N with respect to sulfuric acid [11,12].

/109

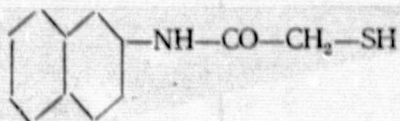
Molybdenum can be separated from tungsten by extraction with acetylacetone in 2 N sulfuric acid [13].

Recently, sulfur-containing organic reagents, which form insoluble compounds with the metals of the hydrogen sulfide group, have

been used in practice in place of hydrogen sulfide (a poisonous gas), viz. thioacetamide, thionalid, thioxine, bismuthiol, sodium diethyldithiocarbamate, dithizone, etc. They are used to precipitate the elements or for extraction [1,8,10].

We pause briefly on two variations of the separation of molybdenum and tungsten: precipitation of the molybdenum with thionalid and extraction of the molybdenum with a mixture of chloroform with acetylacetone.

Thionalid



precipitates many

elements in solutions of mineral acids: arsenic, antimony, tin, gold, palladium, copper, silver, mercury and bismuth. Only thallium is precipitated in an ammoniacal solution in the presence of complexing agents. There are no data in the literature on the precipitation of tungsten and molybdenum. According to our observations, molybdenum is completely precipitated by thionalid in a mineral acid medium at a pH of 1-3. The complete precipitation of molybdenum is reached in the presence of a two-fold excess of the thionalid.

Tungsten does not react with thionalid and it remains in the solution in which it can be determined gravimetrically or polarographically (Table 1). This method for separating molybdenum and tungsten gives the most accurate results for alloys which contain 25% tungsten or more (Table 2).

A sample weighing 0.1-0.2 g is placed in a platinum crucible and treated with a mixture of hydrofluoric and nitric acid. The solution in the crucible is evaporated to dryness and the residue is treated twice with nitric acid and once with water. Each time the process of evaporating to dryness is repeated. The dry residue is fused with 1.5 g of sodium carbonate and the button is leached in water and then the solution is diluted to 150-200 ml with water. A pH of 1 is reached with hydrochloric acid and 1-3 ml of a 10% solution of ammonium persulfate and 30-40 ml of a 2% acetic acid solution of

TABLE 1

/110

DETERMINATION OF TUNGSTEN IN TUNGSTEN-MOLYBDENUM ALLOYS

Charge for alloy		W found, %	Relative error, %	Method used to separate W from Mo	Method used for the Determination
W	Mo				
75.0	25.0	74.4	-0.8	Precipitation w/thionalide	Gravimetric with β -naphthoquinoline
75.0	25.0	75.1	+0.1	Same	Same
50.0	50.0	49.8	-0.4	"	"
50.0	50.0	48.7	-2.6	"	"
50.0	50.0	49.3	-1.4	"	"
50.0	50.0	50.7	+1.4	"	Polarographic
25.0	75.0	24.0	-3.2	"	Gravimetric with β -naphthoquinoline
25.0	75.0	24.3	-2.8	"	Polarographic
25.0	75.0	24.6	-1.6	"	Photocolorimetric
25.0	75.0	24.3	-2.8	Extraction	Same
33.0	97.0	2.85	-5.0	"	"
3.0	97.0	2.90	-3.3	"	"
1.5	-	1.5	0.0	"	"
1.5	-	1.44	-4.0	"	"
1.5	-	1.58	+5.3	"	Polarographic

the thionalid are added. The precipitate is stirred vigorously and the solution, with the precipitate, is transferred to a 250 ml volumetric flask, brought to the mark with water, and stirred again. It is then allowed to stand for 30 min. so the precipitate can settle out. The solution with the precipitate is filtered through a dry filter into a dry beaker. For the gravimetric determination of the tungsten, an aliquot portion of the solution, 50 or 100 ml, is heated to 60-70°C and the tungsten is precipitated with 30 ml of a 1% solution of β -naphthoquinoline. The solution with the precipitate is placed on a water bath to coagulate the precipitate. The precipitate is filtered off, washed two or three times with a 1% solution of hydrochloric acid, and placed in a weighed porcelain crucible. It is dried and ignited at 500-600°C.

For the polarographic determination of tungsten, a 10 ml aliquot part of the solution is placed in a heat resistant beaker and the organic material is destroyed with a mixture of sulfuric and nitric acid. The solution is then evaporated until a light-yellow-colored residue is obtained. The residue is dissolved in concentrated hydrochloric acid and the tungsten is determined polarographically against a back-

ground of an 8 N solution of hydrochloric acid. The half-wave potential for the tungsten is -0.42 V.

The molybdenum is extracted with a mixture of chloroform and acetylacetone from a less acid medium than that for the extraction with the more costly reagent - acetylacetone.

A sample of the alloy weighing 0.5 g is placed in a platinum crucible and treated with a mixture of hydrofluoric and nitric acid. The solution in the crucible is evaporated to dryness and the residue is treated twice with nitric acid and once with water. Each time the evaporation to dryness is repeated. The dry residue is fused with 3 g of sodium carbonate. The button is leached with water and the solution is transferred to a 100 ml volumetric flask and brought to the mark with water. Twenty milliliters of this solution is transferred to a separatory funnel and enough hydrochloric acid is added to make the solution 2 N. To this we add 20 ml of an organic mixture (acetylacetone + chloroform, 1:1) and the solution is extracted for 3 min. After the layers have separated, the lower organic layer is transferred to another separatory funnel and the aqueous layer is transferred to a beaker. After extracting the molybdenum, the organic phase is washed with 30 ml of 2 N hydrochloric acid and the organic layer is removed. The aqueous layer is added to the beaker with the main aqueous phase and boiled for 5-10 min. to remove the organic materials from the solution. /111

If more than 5% tungsten is present in the alloy it is determined gravimetrically. For this the aqueous layer is diluted with water to 100-150 ml and the tungsten is precipitated with a 1% solution of β -naphthoquinoline with heating, as described above.

If the tungsten concentration is less than 5%, the aqueous layer, after extracting the molybdenum, is boiled for 5 min. to remove the organic material and then transferred to a 100 ml volumetric flask. An aliquot portion is taken and the tungsten is determined in the form of the thiocyanate complex by the photocolometric method using the FEK-N-57 photocolometer. The optical density of the thiocyanate complex of tungsten is measured in cells with $l =$

TABLE 2
AMPEROMETRIC DETERMINATION
OF TUNGSTEN

Taken, g	Found, g
0.034	0.0336
0.052	0.053
0.026	0.0258
0.068	0.069
0.039	0.040
0.014	0.0144

TABLE 3
DETERMINATION OF TUNGSTEN
IN ALLOYS

Concentration in the charge, %	Found, %	
	Thiocyanate Method	Amperometric Method
4.50	4.54	4.48
5.60	5.74	5.66
10.20	10.05	10.12
15.40	15.12	15.29
20.60	20.76	20.46

30 mm with a No. 2 light filter (blue). A freshly prepared solution of titanium trichloride is used as the reducing agent.

For the polarographic determination of the tungsten, the aqueous layer, after extracting the molybdenum, is placed in a 50-70 ml beaker and evaporated to dryness. The residue is treated with a mixture of sulfuric and nitric acid to remove the organic material. The residue is then dissolved in 25 ml of concentrated hydrochloric acid, transferred to a 100 ml volumetric flask and diluted to the mark with water. An aliquot portion of the solution is taken, such that it contains no more than 10 mg of tungsten, and the tungsten is determined polarographically against a background of 8 N hydrochloric acid. The half-wave potential for the tungsten is -0.42 V.

/112

β -Naphthoquinoline can be used both for the gravimetric and for the amperometric determination of tungsten. By 1946, V. Sandberg developed a method for the amperometric titration of cadmium with β -naphthoquinoline in a 0.5 M solution of sulfuric acid in the presence of potassium iodide at a potential of -0.9 V.

An attempt was made to use β -naphthoquinoline as the titrating solution to determine large amounts of tungsten. The titration was done at a pH of 3.5 for solutions of sodium tungstate. Solutions of phosphoric acid, which forms the readily soluble phosphotungstate complexes with tungsten, was used to acidify the sample to the required pH. The migration currents were suppressed with potassium

iodide. The amperometric titration was carried out on solutions of sodium tungstate with a known tungsten concentration (Table 3). In all cases the volume of the solution for the titration was 40 ml. To each sample 2 g of potassium iodide was added and the solution was titrated in the cold with a 0.5% aqueous solution of β -naphthoquinoline at a voltage of -0.86 V.

Alloys containing 0.5-60% tungsten, along with titanium, aluminum, iron, manganese and iron, were analyzed in addition to the synthetic mixtures.

A sample of the alloy weighing 0.5 g was dissolved in 40 ml of sulfuric acid (1:3) with heating. After the pieces were dissolved, nitric acid was added dropwise until SO_3 vapors formed. The residue was cooled, dissolved in 50 ml of water with heating. The acid solution was transferred into a 500 ml volumetric flask, which contains 30 ml of 20% sodium hydroxide, and stirred. After cooling water is added to the mark and the mixture is again stirred, the mixture is filtered through a dry filter into a dry beaker and 10-15 ml of the solution is used for the determination. This is neutralized with dilute (1:10) phosphoric acid, diluted with water to 35-40 ml, and 2 g of potassium iodide are added. The resulting mixture is titrated with a 0.5% solution of β -naphthoquinoline.

CONCLUSIONS

1. Methods have been developed for determining tungsten in tungsten-molybdenum alloys. For tungsten concentrations of 25% and more, a method was used which is based on the precipitation of the molybdenum with thionalide and then the tungsten is determined gravimetrically or polarographically. For 1.5% tungsten and more a method is used which is based on the extraction of the molybdenum with a mixture of acetylacetone and chloroform (1:1) followed by gravimetric or polarographic determination.

2. The accuracy of the gravimetric and polarographic methods (tungsten concentration of 25% and more) is $\pm 1.5\%$. For the polarographic and photolorimetric determinations (tungsten concentration

/113

less than 25%) it is $\pm 3\%$ (relative).

3. The possibility was demonstrated of using the amperometric method to determine tungsten by titrating with β -naphthoquinoline. The relative accuracy of the method is $\pm 2\%$ for tungsten concentrations of 0.5-20%.

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The individual determination of large amounts of molybdenum and tungsten for their combined presence is a complicated analytical problem. The existing methods are long and require the final, colorimetric determination of each component. Complete separation of these elements is not achieved by acid hydrolysis of tungsten even with sulfuric acid.

We have shown that the separation of tungsten and molybdenum with β -naphtholquinoline in highly acid solutions is also proscribed by a certain molybdenum concentration above which the molybdenum coprecipitates with the tungsten.

/114

The work of Gopala Rao¹ is of much interest with respect to the determination of molybdenum in the presence of tungsten. He was the first to determine the oxidation-reduction potential of the $\text{Mo}^{6+}/\text{Mo}^{5+}$ pair in phosphoric acid of different concentrations.

A comparison of the potentials for the $\text{Mo}^{6+}/\text{Mo}^{5+}$ and $\text{Fe}^{3+}/\text{Fe}^{2+}$ pairs showed that up to a concentration of 5.8 M phosphoric acid and the $\text{Fe}^{3+}/\text{Fe}^{2+}$ pair has a higher oxidation reduction potential than the $\text{Mo}^{6+}/\text{Mo}^{5+}$ pair. For orthophosphoric acid concentrations greater than 11 M, the difference between the potentials for $\text{Mo}^{6+}/\text{Mo}^{5+}$ and $\text{Fe}^{3+}/\text{Fe}^{2+}$ becomes quite large, which makes it possible for the divalent iron to reduce the hexavalent molybdenum at room temperature. The dependence of the electrokinetic potential for $\text{Mo}^{6+}/\text{Mo}^{5+}$ and $\text{Fe}^{3+}/\text{Fe}^{2+}$ on the orthophosphoric acid concentration is shown in Fig. 1.

For orthophosphoric acid concentrations of about 13 M, the difference in the potential between the two pairs is large; therefore, in

*VNIITS

¹Gopala Rao G. - Talanta, 1963, 10, 1047

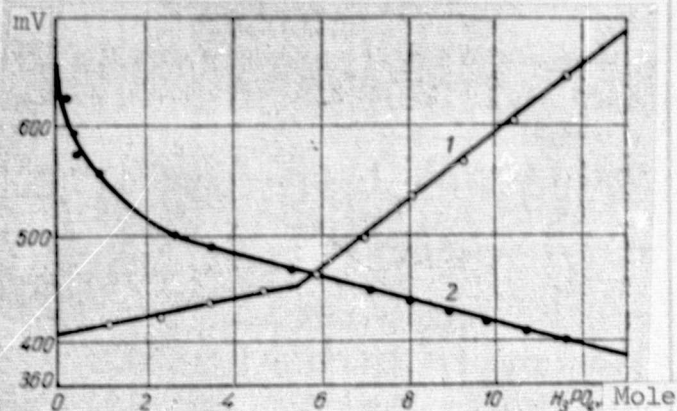


Fig. 1. The dependence of the electrokinetic potential for Mo⁶⁺/Mo⁵⁺ (1) and Fe³⁺/Fe²⁺ (2) on the orthophosphoric acid concentration.

solutions with a known molybdenum concentration in the following way: A solution containing 1-20 mg of molybdenum was diluted with water to 30 ml and 60 ml of orthophosphoric acid and 1 ml of a 0.1% solution of methylene blue were added and the mixture was titrated with a 0.05 M solution of Mohr's salt in a stream of carbon dioxide. After each addition of two drops of a titrated solution of Mohr's salt, the solution was stirred carefully for 15 sec. and more of the titrated solution of Mohr's salt was added. In titrating small amounts of molybdenum (1-10 mg) the solution became a pale blue towards the end of the titration and at the equivalence point it became colorless. For molybdenum concentrations of 10-20 mg, the color of the solution, which was blue at the beginning of the titration, became pale blue at the end. The results of the experiments are given in Table 1. The relative error of the determination does not exceed 9% for determining low molybdenum concentrations (about 3 mg) and for higher concentrations it is no greater than 3%.

In determining molybdenum in solutions containing different molybdenum to tungsten ratios (Table 2), the sample solution was diluted with water to 30 ml and then the method used to determine molybdenum without the presence of tungsten was used. For molybdenum concentrations up to 5 mg, the relative error does not exceed 6%, and for concentrations up to 24 mg, it does not exceed 4%.

13 M acid the hexavalent molybdenum oxidizes the divalent iron rapidly. The oxidation-reduction potential for Mo⁶⁺/Mo⁵⁺ in a 13 M solution of orthophosphoric acid is 0.685 V and that for Fe³⁺/Fe²⁺ is -0.386 V. The reducing potential for methylene blue and thionine are -0.55-0.56, respectively. Therefore, these indicators can be used to titrate molybdenum with a solution of Mohr's salt.

/115

/116

TABLE 1

DETERMINATION OF MOLYBDENUM BY TITRATION WITH A FERROUS AMMONIUM SULFATE SOLUTION [Mohr's Salt].

Mo Taken, mg	Mo Found, mg	Difference	Relative error, %
1.02	0.97	-0.05	-4.9
1.58	1.44	-0.14	-8.9
2.52	2.74	+0.22	+8.7
3.16	3.28	+0.12	+3.8
4.74	4.80	+0.06	+1.2
6.30	6.40	+0.10	+1.5
7.90	8.09	+0.19	+2.4
11.06	11.36	+0.30	+2.7
11.98	11.84	-0.14	-1.1
15.80	15.55	-0.25	-1.5
19.00	19.11	+0.11	+0.6
19.50	19.56	+0.06	+0.3
20.00	19.84	-0.16	-0.8

TABLE 2

VOLUMETRIC DETERMINATION OF MOLYBDENUM IN THE PRESENCE OF TUNGSTEN (69.6 mg)

Mo Taken, mg	Mo Found, mg	Error in the Determination	
		mg	%
1.02	0.97	0.05	-5.0
2.27	2.32	0.05	+2.2
3.00	3.20	0.20	+6.6
3.47	3.68	0.21	+6.0
5.53	5.36	0.17	-3.0
7.90	8.09	0.19	+2.4
7.94	7.99	0.04	+0.5
11.85	12.30	0.45	+3.8
14.22	14.76	0.54	+3.8
15.80	15.40	0.40	-2.5
15.80	15.90	0.10	+0.6
17.38	17.83	0.45	+2.5
19.75	20.20	0.45	+2.2
22.23	22.14	0.09	-0.4
23.82	23.98	0.16	+0.6

The effect of sulfuric and hydrochloric acid on determining molybdenum in solutions containing tungsten and molybdenum was determined by adding 5 ml of the given acid to the solution along with the orthophosphoric acid. The experimental results are given in Table 3. From these we can see that sulfuric or hydrochloric acid do not interfere with the titration of molybdenum.

TABLE 3

DETERMINATION OF MOLYBDENUM IN THE PRESENCE OF SULFURIC OR HYDROCHLORIC ACID (Tungsten Concentration in all of the Experiments, 69.6 mg)

Molybdenum taken, mg	Acid	Mo Found, mg	Difference, mg	Relative error, %
3.00	Hydrochloric	3.06	0.06	+2.0
5.53	"	5.60	0.07	+1.2
7.90	"	8.12	0.22	+2.7
11.91	"	12.00	0.08	+0.7
13.43	"	13.58	0.15	+1.1
15.80	"	15.64	0.16	-1.0
3.95	Sulfuric	4.10	0.05	+1.3
7.90	"	8.37	0.47	+5.8
11.91	"	12.00	0.08	+0.7
15.80	"	15.80	0	0

A decrease in the concentration of the phosphoric acid makes the titration less clear-cut. Ammonium salts have no effect, but the presence of chromium, manganese and vanadium in large amounts interfere with the determination of molybdenum.

The molybdenum can also be determined by potentiometric titration in 13 M phosphoric acid. A platinum wire serves as the indicator electrode and a calomel electrode is the comparison electrode. The equilibrium potential is reached faster if the solution is stirred. The titration conditions are the same as for the volumetric determination. /117

For molybdenum concentrations up to 20 mg, the potential has an abrupt jump. However, for concentrations greater than 20 mg, no large jump is observed in the potential and the end of the titration could only be judged from how little it changed near the equivalence point. In this case, 1 ml of methylene blue indicator was added to the solution to fix the potential jump at the equivalence point.

The indicator lost its color somewhat before the equilibrium potential was reached. The presence of sulfuric or hydrochloric acid in the solution did not interfere with the titration. We can see from the data on the potentiometric titration of molybdenum in the presence of tungsten, which are given in Table 4, that it gives good results.

TABLE 4

Mo Taken, mg	Mo Added, mg	Mo Found, mg	Error in the determination	
			mg	Relative %
9.65	28.42	9.60	0.05	-1.0
9.65	48.63	9.60	0.05	-1.0
19.30	28.42	19.20	0.1	-0.5
28.95	42.63	28.80	0.15	-0.5
48.25	42.63	48.48	0.23	+0.5

TABLE 5

Tungsten concentration	Method		
	Gravimetric	Volumetric	Potentiometric
50.2	4.90	4.80	4.85
16.5	2.66	2.74	2.60

Data are given in Table 5 on the determination of molybdenum in two tungsten concentrations by the volumetric and gravimetric methods.

CONCLUSIONS

1. Volumetric and potentiometric methods have been developed for the determination of molybdenum in the presence of tungsten based on the oxidation reduction reaction $\text{Mo}^{6+}/\text{Mo}^{5+}$ and $\text{Fe}^{3+}/\text{Fe}^{2+}$ in 13 M orthophosphoric acid solutions.

2. These methods can be used to determine molybdenum in the presence of tungsten in various solvents as well as in ores and concentrates.

PHOTOMETRIC DETERMINATION OF BORON IN NICKEL AND
TITANIUM BORIDES USING THE MAGNESON I REAGENT
IN AN ALKALINE MEDIUM

/117

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The classical volumetric method of titration with a solution of sodium hydroxide in the presence of glycerine or mannite [1,2,6] is used to determine boron in the borides of refractory metals and in ores and minerals, and steels in which its concentration is greater than 0.2%. If its concentration is less than 0.05%, colorimetric methods are used with guinalizarin, carminic acid aresenazo 1, etc. for which the reaction with boron takes place in concentrated sulfuric acid [1,4,7].

/118

Studies have been published on new organic reagents for determining boron in weak acid solutions [3,5]. N. S. Polyektov [7] indicated that boron should give color reactions in slightly acid and alkaline solutions with organic reagents of the hydroxyazo dye type which have an OH group in the para position with respect to the azo group in one ring and in the ortho position in the other.

N. S. Polyektov suggested using n-resorcin for the colorimetric determination of boron in an acetic acid medium. Hardly any methods have been suggested for the colorimetric determination of boron in alkaline media. In this work a method is given for the photocolometric determination of boron with the reagent Magneson I

in slightly alkaline media.

Its solutions have a brownish-red color at a pH of 8-10.5 and a violet color at pH of 12-13. We have shown that boron forms a yellow-colored compound with Magneson I in a slightly alkaline medium. The effect of the solution's pH on the color of the boron compound with Magneson I is shown in Fig. 1, from which it follows that the reaction of boron with Magneson I to form a colored compound can only

/119

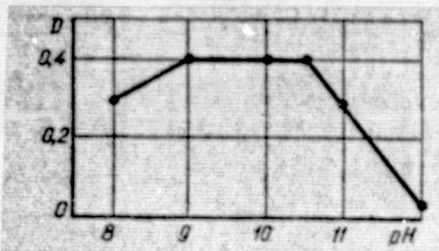


Fig. 1. Effect of the pH on the optical density of solutions of the compound of boron with Magneson I.

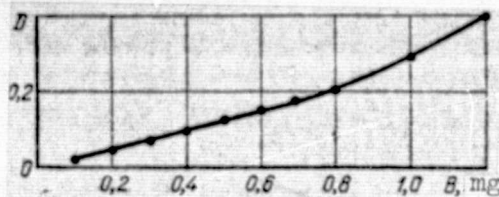


Fig. 2. Standard curve for the determination of boron with Magneson I (0.1-1.2 mg boron in 100 ml of solution).

take place in a slightly alkaline medium with a pH of 8-10.5. The colored compound for boron with Magnesium I is formed at room temperature immediately after the reagent -- Magneson -- is added to a slightly alkaline solution of boron. The color of the boron compound with Magneson I is stable, readily reproducible, and quite suitable for photometric determination. For boron concentrations of 0.11-3.0 mg, the color of the compound that is formed with Magneson I obeys the Lambert-Beer law (Figs. 2 and 3). The solutions of Magneson I in an alkaline medium are intensely colored; therefore, in determining different boron concentrations, different amounts of the solution are used. A standard curve is set up with 6 ml of a 0.05% solution of Magneson I (see Fig. 2) for the photometric determination of 0.2-1.2 mg of boron, with 12 ml (see Fig. 3) for 1.0-2.8 mg, and with 16 ml of reagent for 2.8 mg.

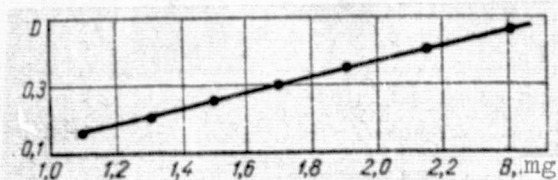


Fig. 3. Standard curve for determining boron with Magneson I (1.1-2.4 mg boron in 100 ml of solution).

The curves for the light absorption in solutions of the boron compound with Magneson I and of the reagent are shown in Fig. 4. The intensity of the color for the boron compounds was measured at 560 μ in the range of a yellow light filter.

The data on the photocolorimetric determination of boron using Magneson I in a slightly alkaline medium are given in Table 1, and they show a good reproducibility of the results for the colorimetric

TABLE 1

EFFECT OF FOREIGN METALS ON THE RE-
ACTION OF BORON WITH MAGNESON I

Added, mg			B Used, mg	B Found, mg
Al	Mo	Ba		
0.5	2.0	0.1	0.54	0.56
0.5	—	0.1	1.29	1.25
—	2.0	0.1	2.16	2.11
—	2.0	0.1	1.94	1.9
0.5	—	0.1	5.0	3.2
—	2.0	0.1	3.0	3.1

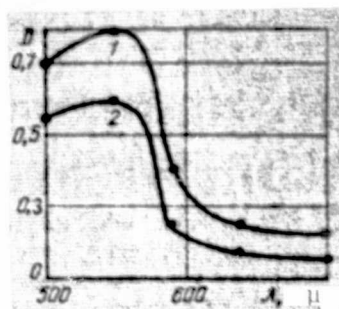


Fig. 4. Light absorption curves
for solutions of Magneson I (1)
and its compound with boron (2)

determination of boron with Magneson I.

Since the reaction of boron with Magneson I takes place in an alkaline medium, in using it for alloys it is necessary to remove or complex the components which form hydrated metal oxides in alkaline media.

EFFECT OF COMPLEXING AGENTS ON THE REACTION OF BORON WITH MAGNESON I

Studies have shown that the presence of tartaric, oxalic, acetic, carbonic and nitric acids, as well as hydrogen peroxide and other oxidizing agents, interferes with the determination of boron with Magneson I and the hydrochloric acid and sulfuric acid ions do not interfere with this determination.

/120

The effect of cations which remain in solution in alkaline media during the analysis of the borides was also studied on the reaction of boron with Magneson I: molybdenum, aluminum and barium (Table 1). The presence of 0.5 mg of aluminum and barium and up to 2 mg of molybdenum does not interfere with the photolorimetric determination of boron with Magneson I.

ANALYTICAL METHOD

One drop 0.01 of a methyl red indicator is added to the solution of boric acid in a 100 ml volumetric flask and the solution is neutralized with 1 N sulfuric acid or 0.1 N sodium hydroxide until the

color changes to a rose. The flask is heated to boiling and then a 0.1 N solution of sodium hydroxide is carefully added dropwise from a burette until the rose color disappears. Using a burette, 6-12 ml of a 0.03% alkaline solution of Magneson I is added to the neutralized solution and 5 ml of a 0.5% solution of gelatin is added. The mixture is stirred and freshly boiled water is added to reach the mark and the mixture is again stirred.

The intensity of the color is measured in a photocolormeter with a yellow light filter in a cell with a layer thickness of L 50 (for 6 ml of reagent) and 20 mm (for 12 ml of reagent). The boron concentration is found from the standard curve:

Boron taken, mg	Boron found, mg	Boron used, mg	Boron found, mg
0.11	0.11	1.94	1.95
0.32	0.32	2.16	2.16
0.54	0.53	2.4	2.3
0.64	0.64	3.0	3.1
1.08	1.1	3.5	3.45
1.29	1.3		

DETERMINATION OF BORON IN NICKEL BORIDES

The color reaction for boron with Magneson I, which takes place in a slightly alkaline medium, was used for the photocolormetric determination of boron in nickel, titanium and chromium borides.

The nickel borides contain up to 30% boron and, depending on the production technology, they may or may not dissolve in hydrochloric acid. Samples weighing 1 g are used to determine the boron in borides which are soluble in hydrochloric acid for boron concentrations of 0.5-2.5% boron. For larger boron concentrations samples weighing 0.2 g are used.

The sample is dissolved in 50 ml of hydrochloric acid (1:1) and heated (but not boiling) for 2-3 hrs. When the sample has dissolved, 5 drops of a 3% solution of hydrogen peroxide are added and the solution is boiled for 15 min. The solution is cooled, transferred to a 200 ml volumetric flask and the excess acid is neutralized

/121

with a 20% solution of sodium hydroxide until a precipitate is formed. Then an excess of 2 ml of sodium hydroxide is added (the solution above the precipitate should be colorless) and the solution is diluted with water to the mark and stirred thoroughly. The nickel precipitates out quantitatively in this procedure. Part of the solution is filtered and 20 ml of the solution is withdrawn into a 100 ml volumetric flask. One drop of methyl red indicator is added and a 1 N solution of sulfuric acid is added dropwise until a clear rose color is obtained. The flask with the solution is heated to boiling and boiled for 5 min. Then a 0.1 N solution of sodium hydroxide is added from a burette until the rose color disappears. The precision of the neutralization is checked by adding a drop of 1 N sulfuric acid to get a rose color and again adding 0.1 N sodium hydroxide carefully, dropwise, until a yellow color appears. Magneson I, 6-12 ml, is added to the neutralized solution and immediately 5 ml of a 0.5% solution of gelatin is added. The mixture is stirred and brought to the mark with freshly boiled water and then it is again stirred. The intensity of the color is measured in a photocolormeter as described above. The boron concentration is found from the standard curve. A blank with all of the reagents is run along with the samples and the optical density of the blank is subtracted as a correction factor. The results of the photocolormetric determination of boron with Magneson I in nickel borides (Table 2) show that boron can be determined photocolormetrically using Magneson I for boron concentrations of 1.0-6% (Experiments 1-7) and greater (8-10). In the latter case, the samples are sintered to convert them to a soluble state.

The data in Table 3 show good reproducibility for the results of the photometric method and good agreement with the results of the classical volumetric method -- titration with an alkali. The method can be used to determine boron photometrically using the color reaction with Magneson I for a boron concentration of 1-23%.

The reaction of boron with Magneson I was used to determine the boron in titanium borides and in alloys based on them with chromium and molybdenum which contain up to 25-29% boron. The titanium boride and its alloys are not soluble in hydrochloric acid and only

TABLE 2
COMPARATIVE DATA ON THE DETERMINATION OF BORON WITH MAGNESON I
AND BY THE VOLUMETRIC METHOD IN NICKEL BORIDES

Number of experiment	Sample weight, g	Boron found volumetrically, %	Boron found photo-colorimetrically, %		
1	1.0	1.08	1.07	1.11	
2	1.0	1.2	1.29	1.25	
3	1.0	1.75	1.83	1.87	
4	1.0	2.05	2.26	2.1	
5	0.2	6.0	5.8	6.08	
6	0.2	8.0	8.1	8.2	
7	2.0	0.38	0.42	0.44	
8	0.1	9.0	9.2	9.4	
9	0.1	12.5	12.1	12.3	
10	0.1	22.4	22.3	22.5	

dissolve in sulfuric acid in the presence of hydrogen peroxide. They can also be converted to the soluble state by fusion with sodium peroxide and sodium hydroxide. In both cases the presence of an oxidizing agent interferes with the reaction between boron and Magneson I.

DETERMINATION OF BORON IN TITANIUM BORIDES WHICH ARE SOLUBLE IN ACIDS

The conditions were found which avoid the effect of the oxidizing agent in determining boron in the titanium borides which are soluble in sulfuric acid with hydrogen peroxide.

A sample of titanium is dissolved 20 ml of sulfuric acid (1:1) and the level of the liquid in the beaker is marked and then 6-10 ml of 30% hydrogen peroxide is added for complete solution of the material. The same amount of the reagent is added to another beaker for the blank. The solutions are heated until the excess hydrogen peroxide is removed (the titanium solution becomes colorless) and they are evaporated to the mark so that no sulfuric acid vapors are lost. The appearance of the sulfuric acid vapors indicated the loss of boron.

After the entire sample has decomposed the solution is transferred to a 200 ml volumetric flask and 10-15 ml of 0.05 N ferrous ammonium sulfate are added (to reduce the remains of the oxidizing agent) and the iron and titanium are precipitated with a 20% solution

TABLE 3
COMPARATIVE DATA ON DETERMINING THE BORON CONCENTRATION IN
TITANIUM BORIDES, %

No. of the Experiment	Sample weight, g	Method		
		Volumetric	Colorimetric (with Magneson I)	
1	0.1 titanium + boron	10,0	10,2	10,5
2	Same	20,0	20,5	—
3	0.1 boride	18,9	19,1	18,8
4	Same	18,9	19,4	19,3
5		24,9	25,1	25,4
6		24,9	25,3	25,8
7		28,9	28,5	28,7
8		28,9	28,6	28,8
9		30,0	29,5	29,8

of sodium hydroxide (no more than 2 ml). The solution is brought to the mark in the volumetric flask with water, stirred, and allowed to stand. The blank is done in the same way. For the colorimetric determination with Magneson I, 20 ml of the initial solution is transferred out as described above. The boron concentration in titanium boride is determined from the standard curve. The results of determining boron in titanium boride are given in Table 3.

The data in Table 3 show that large amounts of boron (up to 28%) in titanium borides can be determined colorimetrically with Magneson I. The error for the method in determining large amounts of boron is +0.5 - 0.7%.

Materials are encountered among the titanium and nickel borides which are insoluble in acids which is due to the method used for their production and the technology for their treatment. Such materials must be fused, but without an oxidizing agent since it interferes with the reaction between boron and Magneson I. In these cases the fusion is best carried out by sintering the sample with barium carbonate. The sample of titanium or nickel boride poured into a high porcelain crucible containing 5 g of barium carbonate. Ten grams of barium carbonate is added. The contents are stirred, being sure to clean the crucible walls with the barium carbonate. Then, after stirring, the mixture is covered with a layer of pure calcium oxide. The heating is

done at 1000°C for 2-3 hrs. in a muffle furnace. The temperature is checked accurately, using a thermocouple. After heating, hydrochloric acid is added to the sintered mass in the cold and then the hydrochloric acid is neutralized with barium carbonate until a slightly alkaline reaction is attained. The mixture is transferred to a 200 ml volumetric flask brought to the mark with water and stirred. A 20 ml aliquot is withdrawn to a 100 ml volumetric flask for the colorimetric determination of boron with Magneson I, as described above. A reagent blank is run at the same time. The experimental results are shown in Table 3 (Experiments 6,8,9) and 2 (Experiments 8-10).

CONCLUSIONS

1. A new method is suggested for the photolorimetric determination of boron with Magneson I in an alkaline medium. The Magneson I reagent allows boron to be determined quantitatively for concentrations of from 0.11 to 3.5 mg in 100 ml of solution in a slightly alkaline medium at a pH of 9-10.5. The optimum conditions were found for the photolorimetric determination of boron and the pH of the solution, the amount of reagent, and the reaction time, the light absorption, the temperature and the effect of a number of cations were determined on the reaction between boron and Magneson I. It was found that the presence of up to 2 mg of molybdenum and up to 0.5 mg of aluminum and barium do not interfere with the determination. The method's sensitivity is 1 µg of boron in 100 ml of solution. /124

2. The conditions were found for the photolorimetric determination of boron with Magneson I in nickel and titanium borides and the alloys of titanium boride.

The method allows boron to be determined photolorimetrically in amounts of 1.0 to 28%. The reaction of Magneson I with boron can be used to determine large amounts of boron in an alkaline medium.

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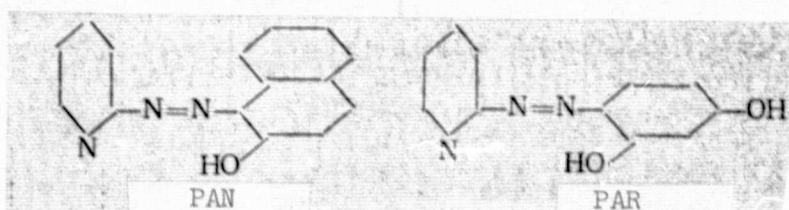
SPECTROPHOTOMETRIC STUDY OF THE REACTIONS OF COMPOUND FORMATION BETWEEN NIOBIUM WITH THE PAN REAGENT

/124

V. I. Kornilova*

The pyridine azo compounds which were first prepared by A. Ye. Chichibabin [1] were not used for a long time in analytical chemistry. Recently, the reagents began to be used as complexometric indicators and for the photometric determination of many elements. The azo compound with the hydroxy group in the ortho-position to the azo group, which is synthesized by the combination of diazotized 2-aminopyridine with 2-naphthol, resorcin, creosol, and other phenols, is of most interest. Most often 1-(2-pyridylazo)-2-naphthol (PAN) and 1-(2-pyridylazo)-resorcin (PAR) are used:

/125



It was found [2] that, depending on the acidity, PAN can be found in three forms in solution: the yellow-green acid form (H_2R^+) at a $pH \leq 2$ which is soluble in water $K_{дис} = 1.26 \times 10^{-2}$, the neutral yellow form (HR) at a $pH \leq 2$ which is insoluble in water and which forms colloidal solutions, and the dissociated red form at a pH of 11, which is soluble in water $K_{дис} = 6 \times 10^{-13}$. The dissociation of the PAN reagent can be represented in the following way [2]:



The most complete information on the use of the pyridine azo compounds in analytical chemistry is given in the review by A. I. Buseva and V. M. Ivanov [3]. Lassner and Puachel [4] studied the reaction of the peroxide complexes of niobium, tantalum and titanium with some metallochrome indicators including PAN. It was found that at

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a pH of 1.5-7 niobium forms a red-violet compound with PAN in the presence of hydrogen peroxide which can be extracted with amyl alcohol.

The purpose of this work was to make a more detailed study of the reaction for the formation of this compound.

Preliminary experiments showed that when hydrogen peroxide is replaced by other complexing agents (Trilon B, tartaric, citric and oxalic acids), no colored compounds are formed.

The starting niobium solution was prepared by fusing niobium pentoxide with potash followed by the dissolution of the potassium niobate in water. The PAN reagent was prepared by dissolving the precise amount in ethyl alcohol.

The formation of the colored compound was studied as a function of the solution's pH which changed from 1 to 5 (Fig. 1). We can see from this figure that the maximum optical density for solutions of the complex compound occurs at a pH of 2.6 and that the complex is stable at pH values of from 2.6 to 4.

The absorption spectra were found for the colored compound of niobium with the reagent PAN and of the reagent itself at a pH of 2.6 (Fig. 2). As we can see from this figure, the greatest difference in the optical densities of the complex and of the reagent are observed at $\lambda = 560 \text{ m}\mu$. From here on, the optical density was measured at this wavelength.

/126

The dependence was studied of the optical density of the compound of niobium with PAN on the hydrogen peroxide concentration. The experiments were set up in the following way. Mixtures were prepared of a calculated amount of potassium niobate and hydrogen peroxide. A calculated amount of alcohol and of the reagent were added to it and the solution was diluted to some fixed volume using a buffer solution with a pH of 2.6. The ratio of niobium to the PAN reagent in the solutions being tested was always Nb: PAN = 1:2. The concentration of the hydrogen peroxide was varied over a wide range (Fig. 3). As we can see from the graph, the addition of the hydrogen peroxide up to a

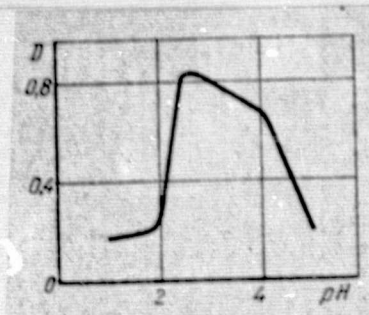


Fig. 1. Dependence of the optical density of a solution of the compound formed by niobium with PAN on the acidity of the solution (niobium concentration - 8×10^{-5} moles/l., of the PAN reagent - 1.6×10^{-4} moles/l., $\lambda = 560 \text{ m}\mu$, cell - 1 cm.

ratio of $\text{Nb}:\text{H}_2\text{O}_2 = 1:250$ results in an intensifying of the solution's color. A further increase in the hydrogen peroxide concentration does not change it and the color only becomes less for a ratio of $\text{Nb}:\text{H}_2\text{O}_2 = 1:2500$. It is apparent that the addition of hydrogen peroxide up to a certain $\text{Nb}:\text{H}_2\text{O}_2$ ratio facilitates the conversion of the niobium into a reactive form.

We know that a solution of PAN in an alkaline medium has a red color. The complex of niobium with PAN is also red; therefore, it may be assumed that only the hydrogen of the hydroxyl group is replaced by the metal in the formation of the colored complex, forming a more polar bond with the oxygen atom of this group than that formed by the hydrogen atom.

The ratio of the reacting components in the niobium - PAN system is determined by the isomolar series method. The total concentration of the components was 3.6×10^{-4} moles. The pH of the solution was 2.6 and all of the solutions contained 0.1 ml of Perhydrol. The optical density of the solutions was measured on a SF-4 spectrophotometer in a cell with a layer thickness of 1 cm. The data on the determination of the composition of the compound formed by niobium with PAN are given in Fig. 4. The maximum on the curve corresponds to a ratio of

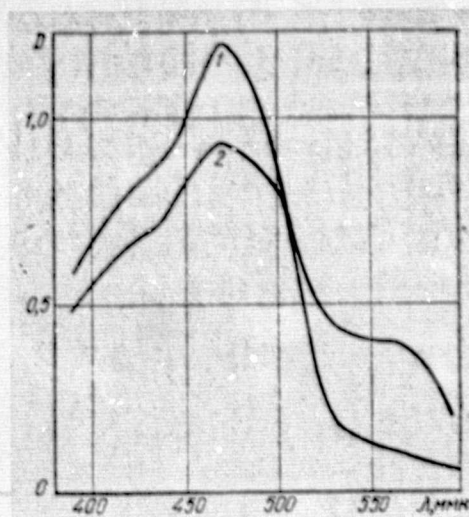


Fig. 2. Absorption spectra for solutions of the PAN reagent and its compound with niobium: 1) PAN reagent at a pH of 2.6, concentration 8×10^{-5} moles/l., 2) compound of niobium with PAN at a pH of 2.6, niobium concentration 4×10^{-5} moles/l.



Fig. 3. Effect of the excess of hydrogen peroxide on the optical density of solutions of the compound formed by niobium with PAN at a pH of 2.6 (the niobium concentration was constant and equal to 8×10^{-5} moles/l., the H_2O_2 concentration varied from 8×10^{-5} - 2×10^{-1} moles/l.

Nb: PAN = 1:2.

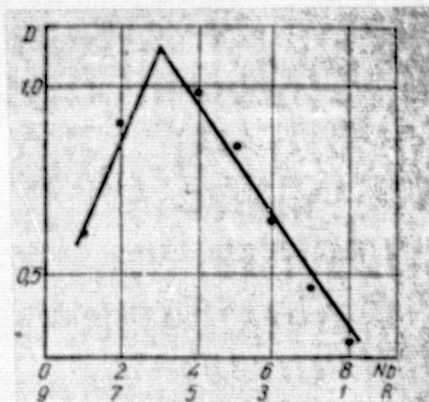


Fig. 4. Determination of the ratio of the reacting components by the isomolar series method in the niobium - PAN system (total concentration of the niobium and PAN - 3.6×10^{-4} moles/l., λ - 560 mμ, cell - 1 cm.

The solutions of the colored compound formed by niobium with PAN obey the Lambert-Beer law for niobium concentrations of 1.8 - 9 μg/ml.

CONCLUSIONS

It was found that niobium forms red colored compounds with PAN in acid solutions (pH from 2.6 to 4) in the presence of hydrogen peroxide with an absorption maximum at $\lambda = 470 \text{ m}\mu$. The composition of the compound corresponds to a ratio of Nb: PAN = 1:2.

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As of now, no description has been given for the determination of small amounts of arsenic (of the order of $1 \times 10^{-4}\%$) in metallic molybdenum and molybdenum salts. The existing spectroscopic method can be used for arsenic concentrations above $5 \times 10^{-4}\%$. The most sensitive and useful method in our case is the determination of arsenic based on the formation of the heteropoly acids $H_3/As(Mo_3O_{10})_4$ followed by its reduction to molybdenum blue. This method can be used for its determination in metallic tungsten [2].

An attempt was made to use the coprecipitation of arsenic with the ferric hydroxide with ammonia for separating arsenic from large amounts of molybdenum. The method did not give good results. Precipitation with $Ca(NO_3)_2$ to remove phosphorus from arsenic did not give good results either. Satisfactory results were found when Alekseyev's method [1] was used to separate arsenic from phosphorus and molybdenum. This is based on the difference in the solubility of the heteropoly acid of arsenic and phosphorus in organic solvents.

The phosphomolybdic heteropoly acid can be readily extracted with a mixture of isobutyl alcohol and chloroform. The arsenomolybdic heteropoly acid is extracted from an aqueous solution with a mixture of isopropyl alcohol, ethyl acetate, and chloroform.

The optimum conditions were found experimentally for determining arsenic in the 0.0001-0.0005 mg concentration range. The optimum volume of the aqueous phase is 40 ml and the volume for the organic solvent mixture is 8 ml. The extraction was made at an acidity of 0.4 N with respect to nitric acid. Under these conditions, up to 0.5 μ g of arsenic can be determined in 25 ml of solution. The optical density of the solution was measured on an FEK-N photocolormeter in

/129

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a cell with a layer thickness of 50 ml using a No. 7 light filter with an effective wavelength of 610 mμ.

The standard curve was set up in the following manner. We added 10 ml of a 25% solution of sodium molybdate to different quantities of a standard solution of arsenic and the mixture was neutralized with nitric acid having a specific gravity of 1.19 and then an excess of 2.5 ml of the nitric acid was added. The solution was transferred to a separatory funnel and diluted to 40 ml with water to remove possible phosphorus impurities. The mixture was shaken and allowed to stand for 10 min. to form the heteropoly acid and then 4 ml of isobutyl alcohol was added to saturate the aqueous solution. Then 4 ml of a mixture of isobutyl alcohol and chloroform (1:3 by volume) was added and the funnel was shaken 30 times. After standing, the lower layer was removed and the extraction was repeated. Under these conditions the phosphorus is completely extracted, as proved in experiments with a standard phosphorus solution.

After extracting the phosphorus complex, 4 ml of a mixture of isobutyl alcohol and ethyl acetate (1:1 by volume) were added and the mixture was shaken vigorously. Then chloroform was added (4 ml) and the solution was agitated by reversing the funnel 30 times. After the layers were separated, the lower layer was filtered into a 25 ml volumetric flask. The extraction was repeated once more. The resulting yellow complex of arsenomolybdic heteropoly acid was reduced in the flask with 0.5 ml of a 0.4% solution of stannous chloride and diluted with isobutyl alcohol to the mark. The optical density of the solution was measured on the photocolormeter. A number of determinations were made for arsenic in solutions of known concentration. The given method gives accurate results (Table 1). Several portions of molybdenum metal were analyzed by this method. The arsenic was determined under the following conditions. One gram of the molybdenum was dissolved in 20 ml of aqua regia on a water bath. The solution was evaporated to dryness and 10 ml of doubly distilled water were added and it was again evaporated to dryness. The molybdic acid is dissolved in 5 ml of 20% alkali, neutralized with nitric acid (sp. g. 1.19) and an excess of 2.5 ml of the nitric acid is added. The solu-

/130

tion is then transferred to a separatory funnel, diluted with water to 40 ml and allowed to stand for 10 min. The extraction was carried out in the same way as for the standard solutions. In analyzing the sample, the molybdenum was used as the reagent needed to form the arsenomolybdic complex (Table 2).

According to spectroscopic analysis, the arsenic in these samples was less than $5 \times 10^{-4}\%$. As we can see from Table 2, the results of determining the arsenic are quite reproducible. The accuracy of the recommended method for determining arsenic was checked by the method of additions. For this, a given amount of the standard arsenic solution was added to the sample of molybdenum. The experimental data are given in Table 3.

TABLE 1
ETERMINATION OF ARSENIC
IN A STANDARD SOLUTION

No. of Experiment	Arsenic taken, mg	Arsenic found, mg	Relative error, %
1	0.0005	0.00055	+10
2	0.0005	0.00035	-30
3	0.0010	0.00085	-15
4	0.0010	0.00095	-5
5	0.0020	0.0018	-10
6	0.0020	0.0019	-5
7	0.0030	0.0032	+7
8	0.004	0.0044	+10
9	0.005	0.0052	+4
10	0.006	0.0067	+12
11	0.007	0.0069	-1.5
12	0.009	0.0095	+6
13	0.010	0.0101	+1.0

TABLE 2
DETERMINATION OF ARSENIC IN MOLYBDENUM METAL SAMPLES
(sample weight - 1 g)

Portion Number	Arsenic Found		Average Arsenic Concentration	
	mg	%	mg	%
261	0.00035 0.00025 0.0032 0.0034	0.000035 0.000025 0.00032 0.00034	0.0003	0.00003
259	0.0027 0.0027	0.00027 0.00027	0.003	0.0003
262	Not found		-	-
257	0.0046 0.0039	0.00046 0.00040	0.0043	0.00043
255	Not found			
256	0.0030 0.0027	0.00030 0.00027	0.0029	0.00029

TABLE 3

DETERMINATION OF ARSENIC IN MOLYBDENUM METAL IN THE PRESENCE OF ADDITIONS OF A STANDARD SOLUTION OF ARSENIC (sample weight of molybdenum - 1 g)

Sample No.	Arsenic concentration in the sample, g	Arsenic added, mg	Arsenic present		Arsenic found		Relative error, %
			mg	%	mg	%	
262	Not found	0.001	0.001	0.0001	0.0011	0.00011	+10
	Same	0.002	0.002	0.0002	0.0017	0.00017	-15
	" "	0.003	0.003	0.0003	0.0033	0.00033	+10
	" "	0.004	0.004	0.0004	0.0042	0.00042	+5
	" "	0.005	0.005	0.0005	0.0048	0.00048	-4
	" "	0.006	0.006	0.0006	0.0061	0.00061	+2
	" "	0.008	0.008	0.0008	0.0080	0.00080	0
	" "	0.009	0.009	0.0009	0.0087	0.00087	-3
	" "	0.010	0.010	0.0010	0.0010	0.00110	+10
261	0.0003	0.002	0.0023	0.00023	0.0022	0.00022	-4
	0.0003	0.003	0.0033	0.00033	0.0030	0.00030	-9
258	0.003	0.001	0.004	0.0004	0.0042	0.00042	+6
	0.003	0.002	0.005	0.0005	0.0051	0.00051	+2
	0.003	0.004	0.007	0.0007	0.0075	0.00075	+7
	0.003	0.005	0.008	0.0008	0.0071	0.00071	-12
	0.003	0.006	0.009	0.0009	0.0093	0.00093	+3
	0.003	0.008	0.011	0.0011	0.0120	0.00120	+10

On the basis of the data in Tables 1-3, it follows that this method for determining arsenic gives a relative error of not more than 12% in the determination.

CONCLUSIONS

1. A photocolorimetric method has been developed for determining arsenic in metallic molybdenum. The method is based on the formation of arsenomolybdenum blue and it can be used to determine concentrations of arsenic of $1 \times 10^{-4}\%$.

2. The lower limit of the sensitivity is 0.5 μg of arsenic in 25 ml.

3. The relative error in the determination does not exceed 12%.

4. The method can be used to determine arsenic in molybdenum anhydride, ammonium molybdate, and other molybdenum preparations.

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CHEMICAL PHASE ANALYSIS OF MIXTURES OF CARBIDES,
BORIDES AND BOROCARBIDES

/132

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In studies of the metal-boron [1,2] and metal-boron-carbon systems [3,7], which showed the presence of a large number of new and as yet unknown individual phases, the method of chemical phase analysis has been widely used. This method is based on the careful study of the chemical composition of the borides, particularly their stability with respect to water and acids, and can be used to isolate individual complex compounds from the mixture obtained in the synthesis. The individual nature of these compounds is then proven by x-ray phase analysis.

The purpose of this work was to demonstrate the effectiveness of this method on concrete examples.

CHEMICAL PHASE ANALYSIS OF SOME BORIDE SYSTEMS

It has been shown [8-10] that the borides have a lower hydrolytic stability and give a greater yield of the borohydrides the greater the amount of metal present in them. This fact can be used in the separation of the various boride phases in systems of the alkaline earth and rare earth metals with boron and in determining the concentration of them in the given samples. These borides were synthesized by mixing the metal powders with the boron and roasting at 800-1300°C. First, all of the known boride phases for these metals were produced and their properties were studied. It was found that the tetraborides of La, Ce and Gd, as well as the hexaborides of these metals and calcium, are almost insoluble in very dilute hydrochloric acid. Only the tetraborides decompose in concentrated hydrochloric acid with boiling. The hexaborides are readily dissolved in nitric acid. The further studies of the hydrolytic decomposition of a large

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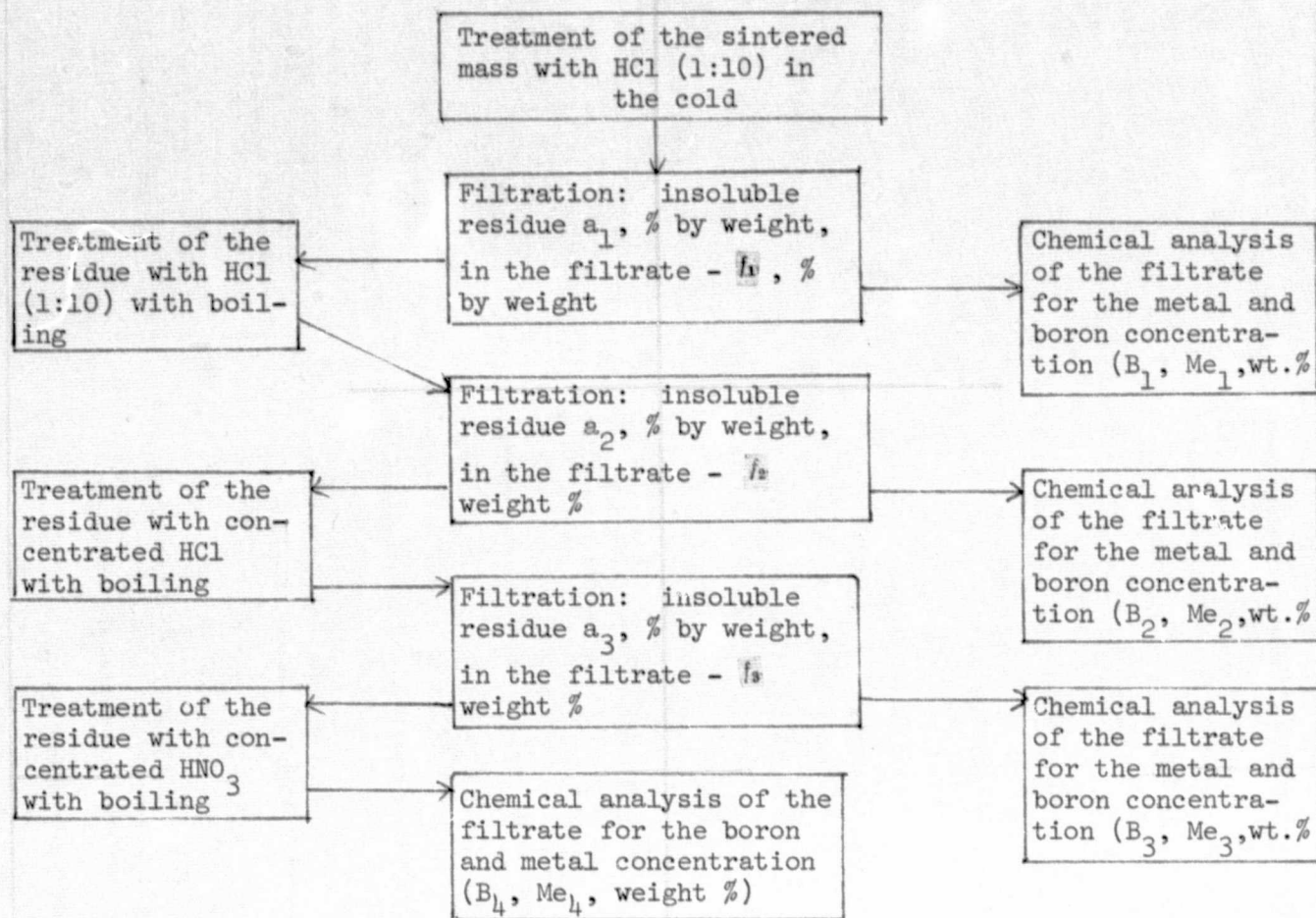
number of boride compositions, synthesized over a wide range of concentrations for the starting materials, showed that the samples produced with an excess of the metal in the reaction mixture, decompose more or less vigorously with the evolution of the borohydrides when treated with dilute hydrochloric acid. This indicated the presence of the lower borides, which were as yet unknown, in the sintered mass masses. These have compositions and properties which are different from MeB_4 and MeB_6 . /134

The experimental data from studying the chemical properties of the boride compositions with alkaline earth and rare earth metals were used to develop a method for their chemical phase analysis (see following page).

According to this method, the products from the reaction of the metals with boron are pulverized, screened and weighed. They are then treated in the cold with very dilute hydrochloric acid (1:10) until the decomposition is finished. The insoluble residue is filtered off and weighed. The filtrate is then analyzed chemically for its boron and metal concentration, using well known analytical methods.

The experimental data showed that the sintered mass from lanthanum and gadolinium with boron undergoes the fastest and most complete decomposition with the dilute hydrochloric acid in the cold. In this process, according to the data in Table 1, the lanthanum and boron and the gadolinium and boron go into solution in amounts which correspond to the atomic ratios 2:1 and 1:1. This indicates that readily decomposed phases having the compositions La_2B and GdB are formed in the La-B and Gd-B systems.

The residues from the sintered masses which do not decompose in dilute hydrochloric acid at room temperature are then treated with HCl (1:10) with boiling. The experiments showed that the samples produced by sintering calcium and gadolinium decompose vigorously as the result of this treatment with the formation of the borohydrides. According to the chemical analysis, in this case the ratio between the metal and boron which go into solution is close to 1:2. From this, it may be concluded that calcium and gadolinium form boride phases with /135



Phase Composition
of the Initial
Product

$$\begin{aligned} \% \text{ Me}_2\text{B} (\text{MeB}) &= (B_1 + \text{Me}_1) \\ \% \text{ MeB}_2 &= (B_2 + \text{Me}_2) \cdot \frac{a_1}{100} \\ \% \text{ MeB}_3 &= (B_3 + \text{Me}_3) \cdot \frac{a_1 a_2}{100} \\ \% \text{ MeB}_4 &= (B_4 + \text{Me}_4) \cdot \frac{a_1 a_2 a_3}{100} \end{aligned}$$

TABLE 1

RESULTS OF THE HYDROLYTIC DECOMPOSITION OF THE PRODUCTS FROM THE REACTION OF SOME ALKALINE EARTH AND RARE EARTH METALS WITH BORON, PRODUCED UNDER OPTIMUM CONDITIONS FOR THE SYNTHESIS OF THE INDIVIDUAL BORIDE PHASES

Atomic Composition of the Reaction Mixture	Reaction Temperature, °C	Dissolved for the Decomposition of the Borides in HCl (1:10), %								Dissolved for the Decomposition of the Borides in Boiling Acids, %							
		At Room Temp.				For Boiling				Concentrated HCl				Concentrated HNO ₃			
		Me	B	Total	At. Ratio Me:B	Me	B	Total	Atomic Ratio Me:B	Me	B	Total	Atomic Ratio Me:B	Me	B	Total	Atomic Ratio Me:B
Ca + 2B	900	—	—	—	—	28,0	17,1	45,1	1:2,21	—	—	—	—	—	54,0	54,0	—
Ca + 4B	1000	—	—	—	—	48,1	26,9	75,0	1:2,1	—	—	—	—	—	24,2	24,2	—
Ca + 6B	1300	—	—	—	—	—	—	—	—	—	—	—	—	37,7	61,5	99,2	1:6,0
La + 2B	900	86,5	3,4	89,9	2:1	—	—	—	—	—	—	—	—	—	9,8	9,8	—
La + 2B	1000	46,4	2,0	48,4	1,9:1	—	—	—	—	39,0	12,6	51,6	1:4,1	—	—	—	—
La + 4B	1000	33,6	1,5	35,1	2:1	—	—	—	—	44,9	14,0	58,9	1:4,0	—	4,2	13,2	1:6,0
La + 6B	1300	—	—	—	—	—	—	—	—	—	—	—	—	67,0	32,2	99,2	1:6,1
Gd + B	1200	87,5	5,8	93,3	1:0,9	—	—	—	—	—	—	—	—	—	—	—	—
Gd + 2B	1300	—	—	—	—	83,5	11,1	94,6	1:1,9	—	—	—	—	—	—	—	—
Gd + 4B	1400	—	—	—	—	—	—	—	—	78,2	21,4	99,6	1:3,9	—	—	—	—
Gd + 6B	1400	—	—	—	—	—	—	—	—	—	—	—	—	69,8	29,8	99,6	1:6,0

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the composition MeB_2 .

The sintered masses of cerium and boron do not decompose noticeably for treatment with dilute hydrochloric acid and, apparently, they do not contain readily hydrolyzable lower borides.

The products which do not decompose in 1:10 HCl are then boiled with concentrated hydrochloric acid. The solid residues which remain are filtered off, weighed and boiled with nitric acid. The hydrochloric and nitric acid solutions are then analyzed for the metal and boron concentrations in them.

According to the data in Table 1, the tetraborides of the rare earth metals dissolve in concentrated hydrochloric acid and the hexaborides of these metals and of calcium dissolve in the nitric acid. The calcium tetraboride, apparently, does not exist. The presence of the lower boride phases for calcium, lanthanum, and gadolinium is also confirmed by x-ray analysis. The lines for these borides are found on the powder diagrams.

CHEMICAL PHASE ANALYSIS OF A NUMBER OF TERNARY Me-B-C SYSTEMS

/136

It has been shown in the studies which have been cited that ternary phases are formed for the reaction of some metals with a mixture of carbon and boron. The borocarbides of the alkaline earth [3] and rare earth metals [4,6], beryllium [7], chromium and manganese [11] have been described. Thus, along with the borides and carbides of the metals and boron carbide, borocarbides exist in the Me-B-C systems.

The method of chemical phase analysis can be successfully used for the separation of these compounds and for determining their composition and concentration in the given samples. Two general schemes for this analysis have been developed in application to ternary systems. One of them was used when the metal forms readily hydrolyzable borocarbides with the boron and carbon, for example, to determine the borocarbides of the rare earth metals. The second is used for the chemical phase analysis of the products which contain chemically stable borocarbides, for example, the borocarbides of beryllium.

Figure 2 for the chemical phase analysis of the sintered masses resulting from the reaction of the alkaline earth metals and some lanthanides (La, Ce, Gd and Eu) with boron and carbon, propose the following sequence of operations:

1. The chemical analysis is made of the initial product for the carbon, boron and metal concentrations ($\text{Me}_1\text{B}_1\text{C}_1$).

2. Determination of the presence of carbides of the MeC_2 type in the sintered masses for the individual samples and the corresponding amounts of metal and carbon (Me_5C_5) based on the amount of acetylene which is formed when the sintered cake is treated with water. It should be pointed out that as a rule such carbides are not present. If they are produced at all, they react with the boron to form the borocarbides.

3. The initial sintered mass is treated with dilute hydrochloric acid. In this case, the borocarbides and the carbides of the metals usually decompose.

The lower borides of the alkaline earth and rare earth metals are unstable in the presence of carbon and their presence is excluded in the given sintered cakes.

As was shown earlier [12], the hydrolysis of the borocarbides in acids is very vigorous and it is accompanied by the formation of solid, liquid and gaseous organic materials, but the latter do not contain acetylene.

4. The residue which does not decompose in hydrochloric acid /138 is filtered off and washed first with water and then with acetone which dissolves the solid organic products from the hydrolysis of the borocarbides.

5. The filtrate is analyzed for the boron and metal concentration (B_2Me_2).

In this scheme, no account is made for the very small amount of boron which remains in the organic material. Such a simplification of the analysis does not have any noticeable effect in determining the composition of the borocarbides.

6. The amount of carbon which is converted into organic material in the hydrolysis of the borocarbides and carbides (C_2) is calculated as the difference between its concentration in the sintered cake before and after hydrolysis.

7. The composition of the borocarbides which have undergone hydrolytic decomposition is calculated using the concentrations found for the metal, carbon and boron (B_2 , Me_2 , C_2) (after subtracting the amount of carbon and metal in the carbides).

8. The undecomposed residue is treated with nitric acid. The hexaboride decomposes and the carbide B_4C and graphite, or a mixture of these, remain in the residue.

9. The nitric acid filtrate is analyzed for its boron and metal concentration (B_3 , Me_3) whose total amount corresponds to the MeB concentration in the sintered cake.

10. The boron present in the residue after treatment with nitric acid is determined and the amount of B_4C which corresponds to it is calculated.

The concentration of free carbon can be determined as the difference between the total carbon and that combined in the form of B_4C .

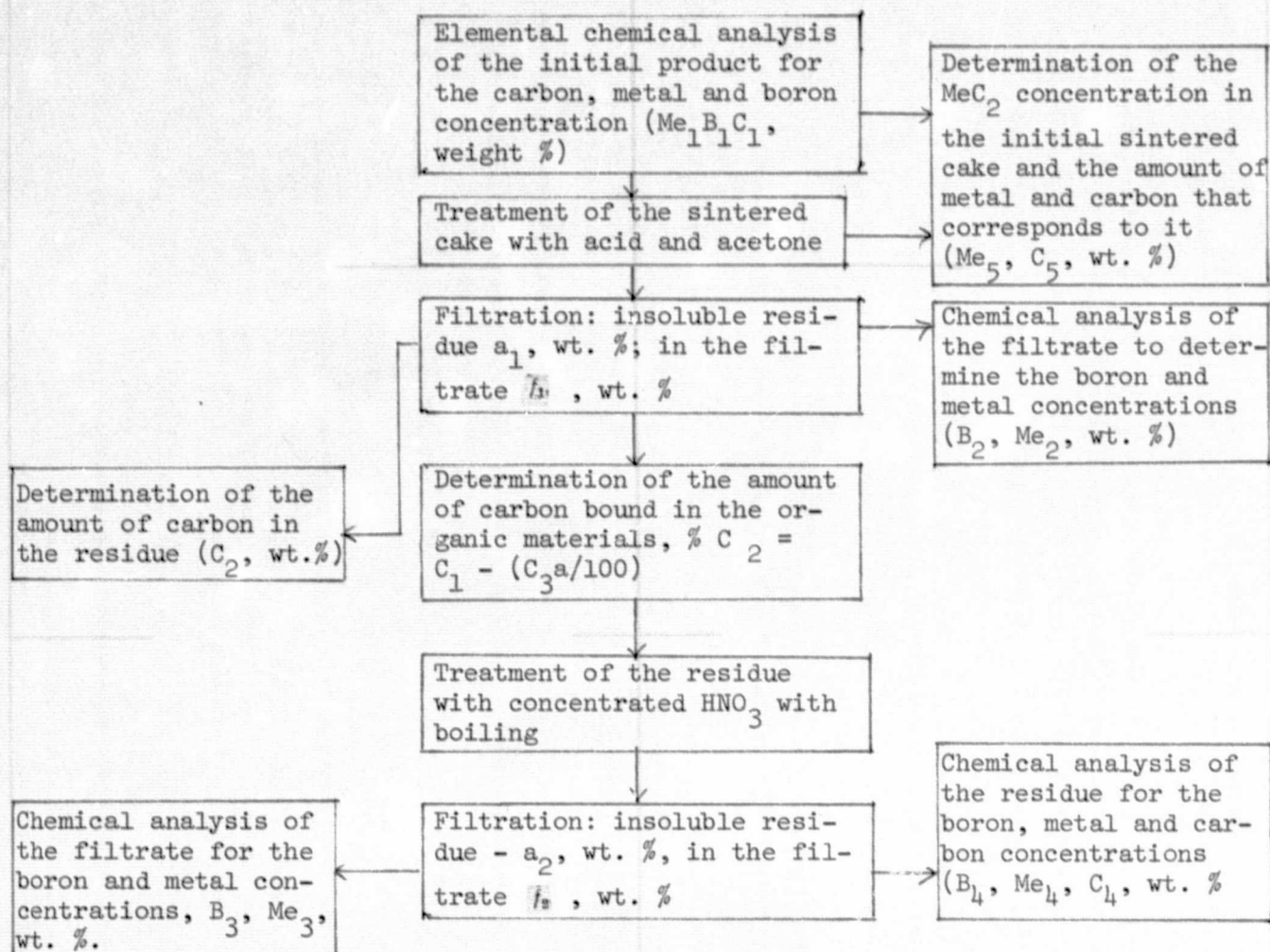
11. In conclusion, the phase composition of the initial product is calculated using the data on the chemical analysis of all of the solid residues and of the acid solutions using the formulae given on page 170.

As an example, the results of the hydrolytic decomposition and chemical phase analysis of the products from the reaction of calcium

/140

CHEMICAL PHASE ANALYSIS OF THE PRODUCTS FROM THE REACTION
OF THE ALKALINE EARTH AND RARE EARTH METALS
WITH BORON AND CARBON

/137



Phase composition of the initial product

$$\% \text{ borohydride} = B_2 + (Me_2 + Me_5) + (C_2 + C_6)$$

$$\% \text{ MeC}_2 = Me_5 + C_6$$

$$\% \text{ MeB}_6 = (Me_3 + B_3) \frac{a_1}{100}$$

$$\% \text{ B}_4\text{C} = \left(B_4 + B_4 \cdot \frac{12}{43.3} \right) \frac{a_1 a_2}{100}$$

$$\% \text{ C}_{\text{carb}} = C_4 - B_4 \cdot \frac{12}{43.3}$$

TABLE 2

RESULTS OF THE HYDROLYTIC DECOMPOSITION OF THE PRODUCTS FROM THE REACTION OF CALCIUM AND LANTHANUM WITH A MIXTURE OF BORON AND CARBON PREPARED UNDER THE OPTIMUM CONDITIONS FOR BOROCARBIDE SYNTHESIS

Atomic composition of the reaction mixture	Reaction Temp., °C	Decomposes for treatment of the sintered mass with 1:4 HCl, %				Atomic ratio Me:B:C (from data on the hydrolytic decomposition)
		Me	B	C	Total	
Ca + 2B + 2C	1300	35,8	10,2	21,8	67,8	1:2:1
Ca + 2B + 4C	1900	35,0	21,1	41,8	97,9	1:2:4
La + B + C	1300	80,5	6,6	7,6	94,7	1:1:1,1
La + B + 2C	1900	78,5	7,2	12,1	97,8	1:1,2:1,8
La + 2B + 4C	1900	64,0	9,5	22,9	96,4	1:1,9:4,1

and lanthanum with boron and carbon are given in Table 2. According to these data, two borocarbide phases are formed in the Ca-B-C system with the compositions CaC_2B and CaC_4B and three are formed in the La-B-C system: LaBC , LaC_2B , and LaC_4B_2 .

The borocarbides of strontium and barium with the same composition as those for calcium and the borocarbides of cerium, neodymium, praseodymium and gadolinium were identified in the same way.

In studying the products which are formed in the Me-B-C system, x-ray phase analyses were also made of the initial products and of the residues which are insoluble in the acids. The resulting data confirmed the results of the chemical phase analysis, particularly the existence of all of the borocarbide phases given in Table 2.

The method of chemical phase analysis of sintered cakes which contain chemically stable borocarbides (using the system Be-B-C as an example (see p. 172)) consists of the following parts:

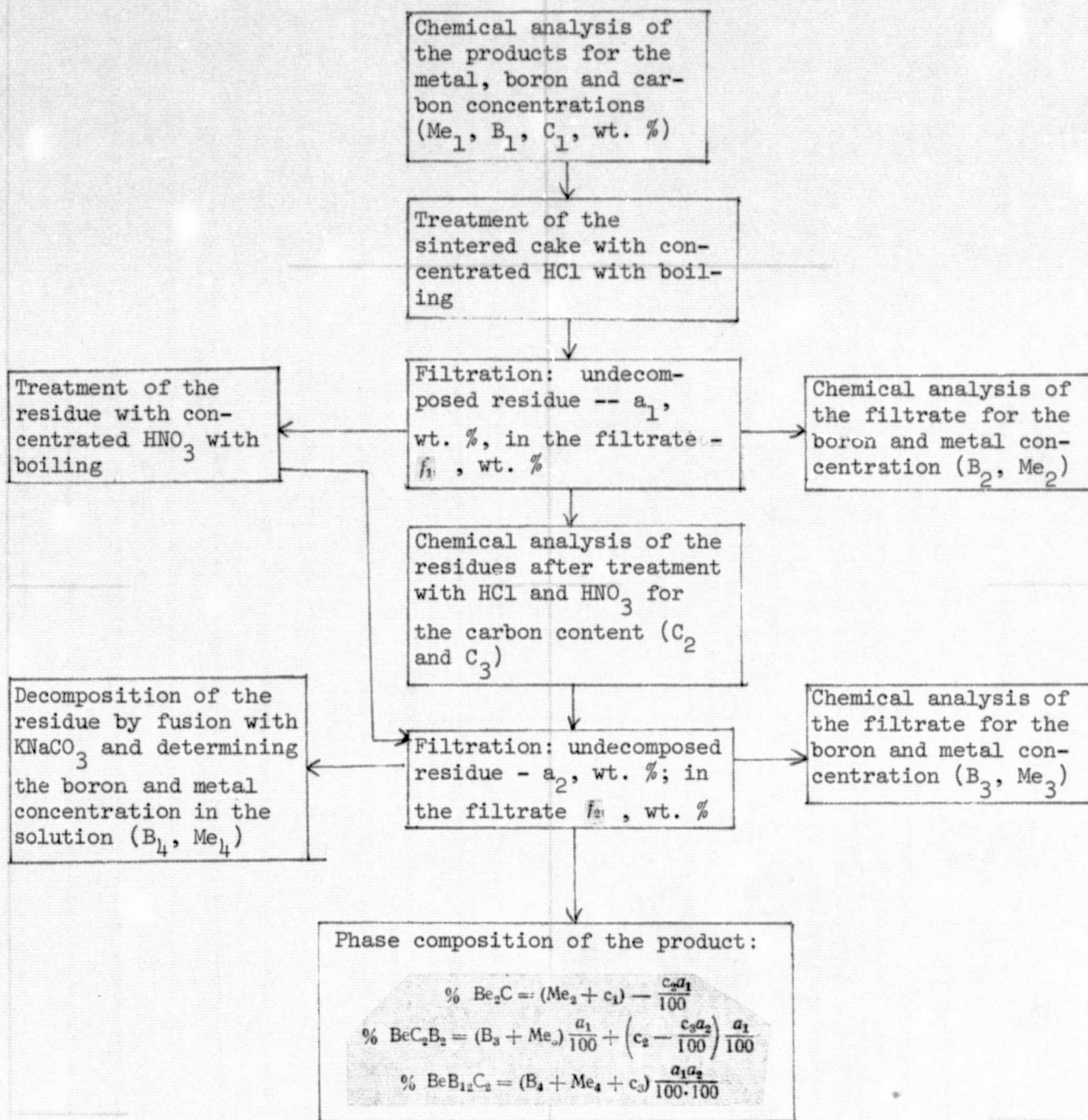
1. The sample product is analyzed chemically for the boron, metal and carbon concentrations (B_1 , Me_1 , C_1).

2. The initial sintered cake is treated with concentrated hydrochloric acid with boiling.

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CHEMICAL PHASE ANALYSIS OF THE PRODUCTS PRESENT
IN CHEMICALLY STABLE BOROCARBIDES

/139



3. The residue which does not decompose in hydrochloric acid is filtered off.

4. The filter is analyzed for the boron and metal concentration in it (Be_2 , Me_2).

5. The product which does not decompose in the hydrochloric acid is boiled with nitric acid. The solid residue is filtered off.

6. The nitric acid filtrate is analyzed for the beryllium and boron concentration in it (Me_3 , B_3).

7. The amount of carbon which corresponds to its amount in the compounds which decompose in the HCl and HNO_3 is calculated from the difference of the concentrations in the products before and after treatment with each acid.

8. The solid residue which is found after treatment of the samples with nitric acid is decomposed by fusion with KNaCO_3 and dissolution of the button in acid. The beryllium and boron in the solution are determined. The carbon concentration in the residue is determined from a separate sample.

9. On the basis of the results of the chemical analysis, the phase composition of the given product is calculated.

According to the experimental data which are given in Table 3, the reaction of the initial sintered cakes with concentrated hydrochloric acid only dissolves the compound which contains only beryllium and carbon ($\text{B}_2 = 0$). In this case, the $\text{Be}:\text{C}$ ratio is close to 2:1, i.e., it corresponds to the carbide Be_2C . Consequently, as a result of the reaction between the boron, beryllium and carbon, no readily hydrolyzable borocarbides are formed.

According to the results of the analysis, a ternary compound which contains beryllium, boron and carbon in the ratio 1:2:2 decomposes in nitric acid, i.e., a borocarbide with the composition BeC_2B_2 .

TABLE 3

RESULTS OF THE ACID DECOMPOSITION OF THE REACTION PRODUCTS FOR BERYLLIUM WITH BORIC AND CARBON
AT 2000°C

Molar composition of the reaction mixture Be:C:B	Decomposes for boiling the cake										Data of the chemical analysis of the products not decomposed in HCl and HNO ₃					
	HCl					HNO ₃										
	Be	C	Total %	Atomic ratio Be:C	Be	B	C	Total	Atomic ratio Be:B:C	Be	B	C	Total	Atomic ratio Be:B:C		
2:1:1	12,3	8,9	21,2	1,8:1	12,8	30,0	30,9	73,7	1:1,8:2	—	—	—	—	—	—	—
1:1:1	30,2	24,8	55,0	1,9:1	5,8	14,2	15,0	35,0	1:2:2	—	—	—	—	—	—	—
1:2:2	—	—	—	—	16,6	38,2	43,6	98,4	1:1,9:2	—	—	—	—	—	—	—
1:2:4	—	—	—	—	6,2	15,2	16,5	37,9	1:2:2	3,5	48,5	10,2	62,2	1:11,7:2		
1:2:12	—	—	—	—	—	—	—	—	—	5,3	79,1	14,1	98,5	1:12:2		

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As the boron concentration in the charge is increased, sintered cakes are formed which mainly contain a compound which is not soluble in either hydrochloric or nitric acid. This substance, which was first purified of B_4C and BeC_2B_2 impurities by acid treatment, contained beryllium, carbon and boron in an atomic ratio of 1:2:12 and, consequently, it is a beryllium borocarbide with the composition BeC_2B_{12} .

The existence of two borocarbide phases for beryllium was confirmed also by the method of x-ray phase analysis. Using the given binary and ternary systems as an example, we can see that chemical phase analysis, amplified with x-ray studies, can lead to well founded conclusions about the phase composition of the given sintered cakes and about the concentration of the individual components in them. This method can also be used to identify new binary and ternary compounds and to determine their composition.

CONCLUSIONS

/142

1. Good results are obtained for determining the phase composition of the products which are formed in some boride and borocarbide systems by using chemical phase analysis based on the different chemical stability of the compounds which are formed in the Me-B and Me-B-C systems during hydrolytic decomposition and reactions with acids.

As an example, a method is studied for the chemical phase analysis of boride compositions of the alkaline earth and rare earth elements. The presence of new phases of the lower borides for these metals was found and their composition was determined.

3. Two general schemes are discussed for the chemical phase analysis of products formed in certain Me-B-C systems. One of them can be used when the metal forms readily hydrolyzable borocarbides with the boron and the carbon, for example, the borocarbides of the alkaline earth and lanthanide metals. The second can be used for the chemical phase analysis of the products which are present in chemically stable borocarbides, for example, the beryllium borocarbides.

4. As an example, the results of the chemical phase analysis

are given for the products of the reaction of calcium and lanthanum, as well as beryllium, with boron and carbon. These confirm the presence of ternary phases in these systems.

5. The conclusions drawn on the basis of the chemical phase analysis should be confirmed by the results of x-ray phase analyses.

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The question of the reaction of borides with carbon and carbides is of great scientific and practical importance. Its practical value is associated with the fact that many borides are used in contact with carbon and carbides which are often used as structural materials.

The study of the reactions of borides with carbon and carbides complements our information about the chemical properties of these compounds and those conversions which take place with them in reactions with carbon and the carbides at high temperatures. The question has not been studied extensively. The literature shows only the work of Glaser [12] on the reaction of the transition metal borides with carbon, in which the high stability of the borides was shown with respect to carbon, and the articles of Benozovskii and his colleagues [14,15] which are devoted to the study of the ternary systems of the Group IV, V and VI elements and the actinoids with carbon along with a few works of G. V. Samsonov and his colleagues on the solid phase reactions of refractory compounds. The studies done at the GIPKh on the ternary systems Me-B-C should also be mentioned, in which the existence of borocarbides of the Group II and III metals and chromium and manganese was demonstrated [3,6]. The formation of these compounds must be taken into account in studying the reactions that take place when borides come into contact with carbon-containing substances.

THE REACTIONS OF THE GROUP II AND III BORIDES WITH CARBON AND CARBIDES

Among the Group II metals, magnesium forms a number of borides-- MgB_2 , MgB_6 , MgB_{12} [9] which decompose ($2000^{\circ}C$) upon roasting with carbon at high temperature. The magnesium volatilizes and the boron reacts with carbon to form B_4C . The magnesium borides do not form ternary compounds with carbon. Only one boride phase has been studied extensively for the alkaline earth metals, i.e., the hexaborides having

*GIPKh

the composition CaB_6 , SrB_6 and BaB_6 . The reactions of the hexaborides with carbon were studied by heating a mixture of the boride and graphite at 1300 and 2000°C [1].

The resulting samples were subjected to chemical phase and x-ray analysis. The chemical analysis showed that they do not react with water and hydrochloric acid and they do not give off even trace amounts of acetylene or organoboron compounds, which should occur if carbides or borocarbides of the metals are formed.

/144

The powder diagrams of the resulting products contained the lines for MeB_6 and graphite. The hexaboride dissolves upon boiling in nitric acid and only graphite remains in the residue. Thus, the mixture of MeB_6 and graphite does not change upon roasting. Consequently, the hexaborides of the alkaline earth metals do not react with carbon.

The high chemical stability of the hexaborides with respect to carbon is also confirmed by the formation of the borides MeB_6 from the reaction of carbides with the composition MeC_2 with boron, and also in the reduction of the oxides of these metals with boron carbide.

In results published earlier [7] of studies at the GIPKh, the existence of alkaline earth diborides was demonstrated. In contrast to the hexaborides, these react rather readily (at 1300°C) with carbon to form ternary phases -- borocarbides with the composition MeC_2B .

Beryllium forms many boride phases, including Be_4B , BeB_2 , BeB_3 , BeB_4 , BeB_6 , BeB_{12} [2,10,11]. They all decompose upon heating in a mixture with carbon. In this case, the borocarbides of beryllium are formed as well as the beryllium carbide -- BeC_2B_2 , hexagonal structure, or $\text{BeB}_{12}\text{C}_2$ (B_4C type of structure).

/149

At high temperatures, the beryllium borides react with beryllium and boron carbides as well as with carbon. Borocarbides are also formed in this case, which have a very high chemical stability (Table 1).

TABLE 1
RESULTS OF THE REACTION OF BERYLLIUM BORIDES
WITH CARBON AND CARBIDES ($t = 2000^{\circ}\text{C}$)

Molar composition of the reaction mixture	Data on the chemical phase analysis of the sintered cakes, %				Results of the x-ray analysis
	BeC ₂ B ₃	BeB ₁₂ C ₂	B ₄ C	Total	
BeB ₂ + 2C	97,0	—	3,2	100,2	Lf* BeC ₂ B ₃
BeB ₆ + 2C	23,3	74,0	—	97,0	Lf* BeC ₂ B ₃ & BeB ₁₂ C ₂
BeB ₁₂ + 2C	—	99,9	—	99,9	Lf* BeB ₁₂ C ₂
BeB ₆ + + B ₄ C + 4C	98,0	—	—	98,0	Lf* BeC ₂ B ₃
BeB ₆ + + Be ₂ C + 5C	96,0	—	—	96,0	Lf* BeC ₂ B ₃
BeB ₆ + + 1,5B ₄ C + C	—	98,0	—	98,0	Lf* BeB ₁₂ C ₂
BeB ₁₂ + + Be ₂ C + 5C	43,0	57,0	—	100	Lf* BeC ₂ B ₃ & BeB ₁₂ C ₂

*Lf — Lines for

For the Group III metals, their reaction with carbon was studied for a number of the hexaborides of rare earth metals, including lanthanum, cerium, gadolinium and europium.

The experimental data showed that the hexaborides of the rare earth elements, like those of the alkaline earth metals, do not react with carbon. Conversely, the lower borides of lanthanum [8] and gadolinium, which were recently prepared react with carbon to form borocarbides of varying composition, specifically MeC₂B, MeC₄B₂ and MeCB.

REACTION OF THE CHROMIUM BORIDES WITH CARBON AND CARBIDES

The data on the chemical phase analysis and of x-ray studies of the products from the sintering of chromium borides having the compositions Cr₂B, CrB, and CrB₂ with carbon and chromium carbides at 1600°C are given in Table 2.

It follows from these data that the different chromium boride phases behave differently with carbon and the carbides. The mono- and diborides do not react with carbon. The lower boride -- Cr₂B -- is unstable in the presence of carbon and is converted to CrB and Cr₃C₂. The sintering of the chromium borides with carbides results in the

TABLE 2
COMPOSITION OF THE PRODUCTS FROM THE REACTION OF CHROMIUM BORIDES
WITH CARBON AND CARBIDES (t = 1600°C)

Molar composition of the reaction mixture	Data of the chemical phase analysis of the sintered mixtures						Data from x-ray analysis	
	CrB	CrB ₂	Cr ₃ BC ₄	Cr ₃ C ₂ +B up to 10 at. %	C	Total		
Cr ₃ B + C	46,1	—	—	53,9	—	100	Lf*	CrB
CrB + C	82,8	—	—	—	17,1	99,9	Lf*	CrB & C
CrB ₂ + C	—	85,0	—	—	15,0	100	Lf*	CrB ₂ & C
Cr ₃ B + Cr ₃ C ₂	—	—	—	100	—	100	Lf*	Cr ₃ C ₂
CrB + Cr ₃ C ₂	—	—	—	100	—	100	Lf*	Cr ₃ C ₂
CrB ₂ + Cr ₃ C ₂	44,8	—	—	54,5	—	99,3	Lf*	CrB & Cr ₃ C ₂
Cr ₃ B + Cr ₃ C ₃	—	—	87,1	12,7	—	99,8	Lf*	Cr ₃ BC ₄
CrB + Cr ₃ C ₃	—	—	81,1	18,9	—	100	Lf*	Cr ₃ C ₂
CrB ₂ + Cr ₃ C ₃	—	—	—	100	—	100	Lf*	Cr ₃ C ₂

*Lf — lines for

formation of products whose powder diagrams do not have any lines of the borides; consequently, the borides react with the carbides. The data from the chemical phase analysis and x-ray analysis showed that in this case either solid solution of the borides in the Cr₃C₂ lattice are formed or a ternary compound, the chromium borocarbide Cr₇BC₄.

REACTION OF MANGANESE BORIDES WITH CARBON AND WITH MANGANESE CARBIDES [3]

Only manganese monoboride is stable in the presence of carbon at high temperatures. The borides Mn₃B₄ and MnB₂ are converted in the presence of carbon into a boride with the composition MnB and the lower borides form borocarbides with carbon.

Alloys having the composition Mn₄B react with carbon when heated to 1300°C to form a mixture of the borocarbides Mn₇BC₂ and Mn₈BC, but for heating above 1500°C only the borocarbide with the composition Mn₇BC₂ is formed.

It follows from the experimental results (Table 3) that borocarbides with the composition Mn₈BC are formed from the reaction of the manganese borides with the carbides at 1300°C and Mn₇BC₂ is formed at

TABLE 3
RESULTS OF EXPERIMENTS ON THE REACTION OF THE MANGANESE BORIDES
WITH MANGANESE CARBIDES AND WITH BORON CARBIDE

Composition of the starting charge molar ratio	Roasting temperature, °C	Phase composition of the reaction products from the chemical and x-ray analysis
$Mn_4B + Mn_{23}C_6$	1300	Mn_8BC
$MnB + Mn_7C_2$	1300	$Mn_7BC_2 + Mn_8BC$
$Mn_3B + Mn_{23}C_6$	1300	Mn_8BC
$Mn_3B + Mn_{23}C_6$	1600	Mn_7BC_2
$Mn_3B + Mn_7C_2$	1800	Mn_7BC_2
$MnB + Mn_7C_3$	2000	$Mn_7BC_2 + C$
$MnB + B_4C$	2000	$MnB + Mn_7BC_2$

higher temperatures.

The manganese borocarbide with the composition Mn_7BC_2 has ferro- /147 magnetic properties and the structure of the hexagonal carbide Cr_7C_2 . The borocarbide Mn_8BC is not ferromagnetic and it has the structure of the complex cubic carbide $Cr_{23}C_6$. Both compounds are hydrolytically unstable. Liquid and gaseous organic products are formed from their decomposition with water and acids.

The fact that the manganese borocarbitides that were prepared have a structure similar to the carbides Mn_7C_2 and $Mn_{23}C_6$ shows that they are derivatives of the carbides and are formed by the replacement of the carbon atoms by boron in the corresponding crystal lattices.

DISCUSSION OF THE RESULTS

A list of the available experimental and literature data is given in Table 4 for the nature of the reaction between borides with carbon. As we can see, the borides react differently with carbon depending on their composition, structure and chemical properties.

All of the lower borides of the metals, e.g., Me_4B , Me_2B_4 , Me_3B_2 , i.e., boride phases with high concentrations of the metals, are unstable with respect to carbon and react with it to form either carbides or borocarbitides.

TABLE 4
STABILITY OF THE BORIDES WITH RESPECT TO CARBON

Metal	Me_2B	Me_3B	Me_4B_3	Me_5B	Me_6B_4	Me_7B_5	Me_8B_6	Me_9B_7	$Me_{10}B_8$	$Me_{11}B_9$
Me	H'	—	H'	—	—	H'	—	H'	H'	H'
Mg	—	—	—	—	—	H	—	H	—	H
Ca, Sr, Ba	—	—	—	—	—	H'	—	—	y	—
Lanthanoids	—	—	—	—	—	H'	—	—	y	—
Ti*	—	H	—	H	—	y	—	—	—	—
Zr*	—	—	—	H	—	y	—	—	—	H
Hf*	—	—	—	y	—	y	—	—	—	—
Ti*	—	—	—	—	—	—	—	H'	y	—
V, Nb*	—	—	—	—	—	—	—	—	—	—
Ta	—	—	H	H	H	y	—	—	—	—
Cr	—	H'	—	H	—	y	—	—	—	—
Mo*	—	H'	—	y	—	y	H	—	—	H
W*	—	H	—	y	—	y	—	—	—	H
Mn	—	H'	—	y	H	H	—	—	—	—

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Remarks: H - unstable in the presence of carbon; H' - unstable in the presence of carbon, forms borocarbides; y - stable in the presence of carbon; *-according to literature data [12,15].

As the boron concentration in the borides increases, which is accompanied by a strengthening of the boron-boron bond, their stability increases. Thus, the hexaborides, which have skeletal structure of boron atoms, are more stable than the diborides and these are more stable than the monoborides, etc. This general rule is clearly evident in the other chemical reactions of the borides, particularly the hydrolytic decomposition, and is applicable, in its general features, to the reactions between the borides and carbon and carbides, also. However, in this case the problem is a little more complicated. There are certain exceptions which are not clear. Thus, for all of the dodecarborides that were studied, an instability with respect to carbon is characteristic. Among the manganese borides, the monoboride is the most stable with respect to carbon. It should be pointed out that a number of other manganese borides, for example, Mn_3B_4 and MnB_2 , are rapidly converted to MnB in the presence of carbon. In addition, since the borides react with carbon at high temperatures, the energy of the boron-boron bond is not always the determining factor and the ratio of the affinity of the metal for boron and for carbon is of importance.

/148

It can be assumed that the further study of the mutual conversions for reactions between the borides and carbides will expose the determining rules.

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CHEMICAL PROPERTIES AND ANALYSIS OF SOME TRANSITION
METAL SULFIDES

/149

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The transition metal sulfides are among the refractory materials whose preparation and physicochemical properties have not been studied extensively. Only the compositions of the phases which are formed in the transition metal — sulfur system during synthesis from the elements are known and some of their crystallochemical properties (type of structure, lattice parameters). There is no information on the stability of the sulfides in various media or their resistance to oxidation. Therefore, it is of interest to study the chemical properties of the transition metal sulfides and to develop, on this basis, methods for their chemical analysis.

Some of the sulfide phases were studied for a number of transition metals: Sc_2S_3 , HfS_2 , V_2S_3 , $\text{NbS}_{1.6}$, TaS_2 , Cr_2S_3 . They were prepared by the action of hydrogen sulfide on the metal powders or their oxides at 1300-1500°C [1,2,3]. The crystallochemical properties and the chemical composition of these sulfides are given in Table 1.

The stability of the sulfide powders was studied in solutions of various reagents for heating for 1 hr. The weighed sample of the sulfide was placed in a tapered flask equipped with a reflux condenser and the reagent was added. The insoluble residue was filtered off through a Schott crucible and the total sulfur and metal concentrations were determined in it. The metal which dissolves in the decomposition of the sulfide is determined in the filtrate. Results were obtained on the stability of Sc_2S_3 , HfS_2 , V_2S_3 , TaS_2 and Cr_2S_3 powders and these are given in Table 2.

/152

The powders of these sulfides are stable in air at room temperature for a long period of time and even for boiling in water. Sc_2S_3 and Cr_2S_3 do not decompose for boiling in alkali solutions. All of the sulfides decompose completely in oxidizing acids (nitric, dilute

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TABLE 1
CRYSTALLOCHEMICAL PROPERTIES OF THE SULFIDES OF SOME
TRANSITION METALS

Sul- fide	Color	Structure	Lattice period			Density, g/cm ³		Chemical com- position, %	
			a	b	c	picno- metric	X-ray	M _{total}	S _{total}
Se ₂ S ₃	Yellow- orange	Ortho- rhombic	5,18	—	—	—	2,96	45,8	55,1
HfS ₂	Brownish- red	Trigonal	3,63	—	5,85	—	—	73,4	25,3
V ₂ S ₂	Black	Hexagonal	6,59	—	22,13	—	—	48,5	51,0
NbS _{1.6}	Black	Hexagonal	3,338	—	17,827	5,9	6,0	62,2	35,4
TaS ₂	Black w/ green tint	Trigonal	3,36	—	5,89	7,1	7,16	73,0	25,5
Cr ₂ S ₂	Black	Trigonal	5,942	—	11,125	3,6	—	52,0	48,6

sulfuric (and in solutions of bromine and hydrogen peroxide.

The oxidizability of the sulfides was also studied by heating them in a stream of oxygen. The particle size of the powders was 270 mesh and the flow rate of the oxygen was 200 ml/min. The degree of oxidation was determined from the amount of sulfur dioxide that is evolved.

The results on the oxidation of the niobium and tantalum sulfides are given in Table 3. It follows from these data that NbS_{1.6} and TaS₂ begin to oxidize at 300°C and total oxidation occurs at 400-500°C and oxidizes completely at 1000°C. The final oxidation products are the metal oxides.

Thus, the scandium, hafnium, vanadium, niobium, and tantalum sulfides, like other refractory sulfides, are unstable for heating in air. The ready oxidizability of the sulfides for heating in air can be used to determine the total concentration of the metal by roasting weighed samples of the sulfide and the amount of sulfur can be determined simultaneously from the amount of sulfur dioxide that is evolved. The sulfur dioxide gas is trapped in an iodine solution in a 3% solution of hydrogen peroxide followed by the titration of the sulfuric /153

TABLE 2

Sulfide	Reagent	Insol- uble Resi- due	Chemical com- position of residue		Metal conc. in soln. %	Remarks	Sulfide	Reagent	Insol- uble Resi- due	Chemical com- position of residue		Metal conc. in soln. %	Remarks
			S _{общ}	Me _{общ}						S _{total}	M _{total}		
Sc ₂ S ₃ HfS ₂ V ₂ S ₃ Ta ₂ S ₅ Cr ₂ S ₃	H ₂ SO ₄ , d = 1,84	0 0 0 0	— — — —	— — — —	— 51,2 73,0 —	Decomposes completely	Sc ₂ S ₃ HfS ₂ V ₂ S ₃ Ta ₂ S ₅ Cr ₂ S ₃	H ₂ O ₂ , 30%	0 0 0 0 92,1	— — — — —	— — — — —	— — 19,7 73,0 3,7	Decomposes completely
Sc ₂ S ₃ HfS ₂ V ₂ S ₃ Ta ₂ S ₅ Cr ₂ S ₃	H ₂ SO ₄ , 1:1	0 0 59,5 99,6 99,3	— — 52,4 22,9 —	— — 39,8 73,0 —	— — 25,7 1,8 0,25	—	HfS ₂ V ₂ S ₃ Ta ₂ S ₅ Sc ₂ S ₃ Cr ₂ S ₃	H ₂ C ₂ O ₄ , 6%	93,0 79,6 99,9	48,4 25,0 0	51,0 73,0 0	3,8 14,8 0	—
Sc ₂ S ₃ HfS ₂ V ₂ S ₃ Ta ₂ S ₅ Cr ₂ S ₃	HCl, d = 1,19	0 0 96,0 98,0 100,1	— — 48,2 24,0 0	— — 51,4 73,0 0	— — 1,7 1,1 0	—	Sc ₂ S ₃ HfS ₂ V ₂ S ₃ Ta ₂ S ₅ Cr ₂ S ₃	Bromine water	0 0 74,8 — 81,2	— — 51,2 — —	— — 47,2 — —	— — 15,0 — 7,75	—
Sc ₂ S ₃ HfS ₂ V ₂ S ₃ Ta ₂ S ₅ Cr ₂ S ₃	HCl = 1:1	0 0 96,3 98,7 99,9	— — 48,1 23,2 0	— — 51,0 72,9 0	— — 1,7 1,0 0	—	Sc ₂ S ₃ HfS ₂ V ₂ S ₃ Ta ₂ S ₅ Cr ₂ S ₃	H ₂ O	99,5 82,4 99,4 99,8 100,0	— — 48,4 48,4 0	— — 51,2 73,0 0	— — 0 0 0	—
Sc ₂ S ₃ HfS ₂ V ₂ S ₃ Ta ₂ S ₅ Cr ₂ S ₃	HNO ₃ , d = 1,4	0 0 0 0 0	— — — — —	— — — — —	— 51,2 73,0 52,0	Decomposes completely	HfS ₂ V ₂ S ₃ Ta ₂ S ₅ Cr ₂ S ₃	NaOH, 40%	0 93,5 97,0 98,0	— 47,7 6,0 0	— 50,5 72,8 0	— 5,5 2,4 0	—
Sc ₂ S ₃ HfS ₂ V ₂ S ₃ Ta ₂ S ₅ Cr ₂ S ₃	HNO ₃ , 1:1	0 0 0 0 0	— — — — —	— — — — —	— 51,2 73,0 52,0	Decomposes completely	HfS ₂ V ₂ S ₃ Ta ₂ S ₅ Cr ₂ S ₃	NaOH, 10%	0 98,6 36,0 99,5 97,9	— 47,6 9,3 0 —	— 55,2 72,9 0 —	— 0 55,5 0 —	—
Sc ₂ S ₃ HfS ₂ V ₂ S ₃ Ta ₂ S ₅ Cr ₂ S ₃	H ₃ PO ₄ , d = 1,21	— — — 1,4 99,9	— — — 22,0 0	— — — 72,9 0	— — — 51,0 0	—							

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TABLE 3
OXIDATION OF THE NIOBIUM AND TANTALUM SULFIDES IN OXYGEN

Temperature, °C	Amount of sulfur oxidized, weight %															
	NbS _{1.6}								TaS ₂							
	Oxidation time, min.															
	10	20	30	40	50	60	90	120	10	20	30	40	50	60	90	120
300	0.7	1.3	2.1	2.2	2.9	3.2	4.5	5.4	1.4	1.4	2.5	2.5	2.5	2.5	2.7	4.0
350	2.3	11.2	14.5	15.9	18.4	21.2	25.9	29.0	Not investigated							

Remarks: Complete oxidation of NbS_{1.6} at 400°C and of TaS₂ at 500°C takes place after 10 min. for TaS₂ and the amount of oxidized sulfur at 400-450°C after 2 hours was 6-5.5%.

acid that is formed with an alkali.

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ANALYSIS OF THE SILICIDES OF THE
GROUP IV-VI TRANSITION METALS

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Modern requirements for analytical chemistry consist mainly of increasing the sensitivity, accuracy and selectivity of the methods for determining the elements. In this plan, the analysis of refractory compounds is of great interest because of the high chemical stability of these samples which are difficult to analyze.

The silicides of the Group IV-VI transition elements are widely used in modern technology. Their analysis is complicated by the high chemical stability of the silicides. In addition, the decomposition may take place with the evolution of gaseous decomposition products - silanes of various composition, which may lead to incorrect results.

The usual methods for decomposing the silicides is fusion with soda and sodium peroxide, which is not completely satisfactory to the analysts since it results either in the waste of platinum, which is scarce (for fusion with soda) or to the possible loss of silica in the form of silanes which often are evolved for fusion with sodium peroxide and in making the analytical procedure more complicated because of the large amounts of iron or nickel that go into solution. It has also been recommended that the insoluble silicates be decomposed by fusing them with a mixture of sodium hydroxide and sodium peroxide in nickel crucibles [2]. Sintering, which is already used for the decomposition of boron carbide and nitride and the borides of some transition metals and some nitrides in determining the nitrogen in them [1,3-5], appears still more promising.

/154

An attempt was made to use this method for the decomposition of the silicides of the Group IV-VI transition elements. Preliminary experiments showed that the silicides of titanium, zirconium, hafnium, vanadium, niobium, tantalum, molybdenum, tungsten and chromium, as well

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as the silicon carbide and nitride, decompose when sintered with a mixture of soda and zinc oxide. It is recommended that the sintering be done in nickel crucibles at 900-1000°C. For this, a sample of the silicide weighing 0.1 g is carefully stirred with 2 g of a 1:1 (by volume) mixture of sodium carbonate and zinc oxide which had been previously dried. A zinc oxide "cushion" (no more than 1 g in weight) is placed on the bottom of the crucible and the sample is covered with the sintering mixture (about 1 g) and the mixture is sintered for 1.5-2 hrs. in a muffle furnace at 900-1000°C. After cooling, the sintered mass is poured into a beaker (if there is a residue in the crucible, it is dissolved in 1:4 sulfuric acid) and 25 ml of concentrated nitric acid is added or it is treated in an appropriate way to determine the chemical reactions that take place during the sintering of the silicides.

All of the silicon from the silicide is found in the aqueous extract for sintering the silicides of titanium, zirconium and hafnium. The zinc oxide in the sintering mixture dissolves in hydrochloric acid. The analysis of the residue which is insoluble in the hydrochloric acid showed that the metal concentration in it corresponds to the stoichiometric value for the dioxide. For the Group VI elements, all of the silicon and the metal go into the aqueous extract or, more properly, into the sodium carbonate solution. The residue which is insoluble in the soda solution, according to the analysis, corresponds to zinc oxide.

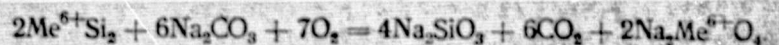
In discussing the processes in the sintering of the Group V silicides, we must take into account the reactions for the formation of the niobate, vanadate and tantalate of the alkali metal, which go into the aqueous extract along with the sodium silicate for vanadium or with potassium silicate and the corresponding niobate and tantalate, and the insoluble residue dissolves in hydrochloric acid and is the zinc oxide which was used to sinter the silicides.

Thus, in sintering the silicides of titanium, zirconium and hafnium, they decompose to form sodium silicate and the oxide of the corresponding metal according to the equation

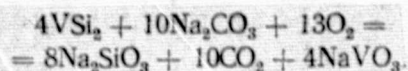
C-2



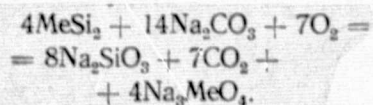
The decomposition for the sintering of the silicides of chromium, tungsten, molybdenum takes place with the formation of sodium silicate and the sodium salt of chromic, tungstic, or molybdic acid, according to the equation /15/



The decomposition for the sintering of the silicides of the transition elements of Group V takes place with the formation of sodium silicate and sodium vanadate (for vanadium silicide) according to the equation



For the decomposition of the silicides of niobium and tantalum, the ortho salts are formed by means of the reaction



Zinc oxide in this mixture only serves to prevent the fusion of the mixture and allows us to carry out the sintering at a higher temperature.

For the sulfuric acid separation of the silicic acid with a single evaporation to SO_3 vapors, some part of it is converted to the soluble state. From the data on the single separation of the silicic acid with its additional determination in the filtrate (Table 1), it follows that the amount of silicic acid which remains in the filtrate varies from 0.2 to 2.5% for a total silica concentration of 50% in the chromium silicide. For a total silicon concentration of 38%, the losses in the acid filtrate are ~ 0.2-1.5% (for zirconium silicide).

The most complete separation of the silicic acid from these data takes place for evaporation of its solutions with nitric acid followed by evaporation to SO_3 vapors (twice) and also with the addition of a gelatin solution in dissolving the salts. In this case, the silicic acid is almost completely separated in the insoluble form from aqueous solutions. It is readily and rapidly filtered through a "white ribbon" filter and is almost insoluble in washing.

The ability of metals to form stable complex compounds with some complexing agent was used as

the basis for separating the silicic acid from the second component of the melt (metal). Thus, in order to prevent the precipitation of the insoluble basic sulfate of trivalent chromium, it is recommended that a saturated solution of oxalic acid be added before the evaporation, which forms quite stable complex compounds with trivalent chromium ions. Oxalic acid in the presence of hydrogen peroxide also favors the retention of niobium, tantalum and tungsten in solution during evaporation to SO_3 fumes. Consequently, in using the sintering method followed by the use of complexing agents and the conditions that were found for the most complete separation of the silicic acid, a reasonable method is given for determining silicon in all of the silicides of the Group IV-VI elements.

TABLE 1
SULFURIC ACID SEPARATION OF
SILICIC ACID IN CHROMIUM
AND ZIRCONIUM SILICIDES, %

Silicide	Amount of silicon found		Total amt. of silicon
	First separation	Second separation	
CrSi_2	49.1	1.10	50.20
	49.4	0.70	50.10
	49.2	1.10	50.30
	48.6	2.00	50.60
	48.2	1.70	49.90
	48.7	2.30	51.00
	49.7	0.30	50.00
	48.6	1.10	49.70
	48.1	1.70	49.80
	48.70	1.40	50.10
ZrSi_2	37.60	0.20	37.80
	36.80	1.50	38.30
	38.30	0.50	38.80
	37.90	0.60	38.50
	38.30	0.40	38.70
	38.30	0.30	38.60
	36.80	1.50	38.30
	37.1	1.10	38.20

/156

SINTERING METHOD

A sample of the silicide weighing 0.1 g is carefully stirred with 2 g of the sintering mixture in a glass weighing bottle and then it is carefully poured into a nickel crucible whose bottom has been

thickly covered with a "cushion" of zinc oxide (weighing no more than 1 g). The weighing bottle is "washed out" with two portions of the sintering mixture (no more than 0.5 g each) and this is placed over the sample and covered by the same mixture. The silicides are sintered at 900-1000°C in a muffle furnace for 1.5-2 hrs. The resulting cake is in the form of a small tablet which, in most cases, is readily removed from the nickel crucible. The nickel from the crucible does not go into the sintered mixture. If the sintered mass sticks to the nickel crucible, it must be cleaned out mechanically.

THE DETERMINATION OF SILICON IN TITANIUM, ZIRCONIUM AND HAFNIUM SILICIDES

The cake which is formed is placed in a beaker which is covered with a watch glass and 25 ml of nitric acid is added (sp. g. 1.43) along with 10 ml of a 30% solution of Perhydrol. If pieces of the cake remain in the nickel crucible, it is washed out with small portions of 1:4 sulfuric acid using total volume of 20 ml. Twenty milliliters of sulfuric acid (sp. g. 1.84) are added to the beaker and the resulting solution is evaporated to SO₃ fumes for 5-10 min. The resulting solution is cooled and 25 ml of hot nitric acid (sp. g. 1.43) and 50 ml of hot water are added to dissolve the salts. Then 20 ml of 1:1 sulfuric acid are added and the solution is again evaporated to SO₃ fumes for no less than 5-10 min. The solution is cooled and then 100 ml of 0.15% solution of gelatin, heated to 60-70°C, is added while stirring to dissolve the salts (without heating on a hotplate) and the silicic acid which is formed is filtered off through a "white ribbon" filter. In mass production work, it is recommended that after the salts are dissolved the silicic acid should be filtered off quickly. It is washed on the filter first with hot hydrochloric acid (1:99) and then 2-3 times with hot water. It is then washed and ignited at 1000°C in a platinum crucible to a constant weight. The ignited precipitate is treated with 2-3 ml of hydrofluoric acid, 2-3 drops of sulfuric acid, evaporated to dryness, ignited and weighed. /157

DETERMINATION OF SILICON IN VANADIUM AND MOLYBDENUM SILICIDES

The cake is placed in a beaker which is covered with a watch

glass and 25 ml of nitric acid (sp. g. 1.43) is added. The residue from the cake is transferred from the nickel crucible to the beaker by washing with a solution of sulfuric acid (1:4) with a total volume of 20 ml and then 20 ml of sulfuric acid is added (sp. g. 1.84) and the solution is evaporated to SO_3 fumes over a period of 5-10 min. The resulting solution is cooled and 25 ml of hot nitric acid is added (sp. g. 1.43) along with 50 ml of hot water to dissolve the salts and 20 ml of sulfuric acid (1:1) and it is again evaporated to SO_3 fumes for no less than 5-10 min. The solution is cooled and 100 ml of a 0.15% solution of gelatin, heated to 60-70°C, is added and the salts are dissolved by stirring (without heating on a hotplate) and the silicic acid which is formed is filtered off through a "white ribbon" filter. It is washed on the filter first with hot hydrochloric acid (1:99) and then 2-3 times with hot water. It is then ashed and ignited at 1000°C in a platinum crucible to constant weight. The ignited precipitate is treated with 2-3 ml of hydrofluoric acid, 2-3 drops of sulfuric acid, and evaporated to dryness, then ignited and weighed.

DETERMINATION OF SILICON IN CHROMIUM SILICIDE

The sintered cake is placed in a beaker which is covered with a watch glass and 25 ml of nitric acid (sp. g. 1.43) is added. The residue from the sintered cake is transferred from the nickel crucible to the beaker by washing with a solution of sulfuric acid (1:4) with a total volume of 20 ml and then 20 ml of sulfuric acid are added (sp. g. 1.84) and 50 ml of a saturated solution of oxalic acid are added. The resulting solution is evaporated to SO_3 fumes for no less than 5-10 min. After cooling, 25 ml of hot nitric acid (sp. g. 1.43) are added to the solution along with 50 ml of hot water to dissolve the salts. Then 20 ml of sulfuric acid (1:1) and 50 ml of a saturated solution of oxalic acid are added and the solution is again evaporated to SO_3 fumes for no less than 5-10 min. The mixture is cooled and 100 ml of a 0.15% solution of gelatin, heated to 60-70°C, are added and the salts are dissolved with stirring (without heating on a hotplate) and the silicic acid is filtered off through a "white ribbon" filter. The operation is continued as described above.

/158

DETERMINATION OF SILICON IN NIOBIUM, TANTALUM
AND TUNGSTEN SILICIDES

/159

The sintered cake is placed in a beaker which is covered with a watch glass and 25 ml of nitric acid are added (sp. g. 1.43) along with 10-15 ml of a 30% solution of Perhydrol, 20 ml of sulfuric acid (sp. g. 1.84), and 100 ml of a saturated solution of oxalic acid, and the solution is evaporated until the niobic, tantalic and tungstic acids are completely dissolved. After cooling, 25 ml of hot nitric acid (sp. g. 1.43), 10 ml of a 30% solution of Perhydrol, and 100 ml of a heated saturated solution of oxalic acid and 20 ml of sulfuric acid (1:1) are added and the solution is again evaporated to SO_3 fumes until the niobic, tantalic and tungstic acids are completely dissolved. The solution is cooled and 10 ml of a 30% Perhydrol solution is added and the mixture is stirred. Then 100 ml of a 0.15% solution of gelatin in saturated oxalic acid heated to 60-70°C, are added with stirring to dissolve the salts (without heating on a hotplate) and the silicic acid is filtered off on a "white ribbon" filter. The residue is washed on the filter first with hot hydrochloric acid (1:99) and then 2-3 times with hot water. Then it is ashed, and ignited to 1000°C in a platinum crucible to constant weight. The ignited residue is treated with 2-3 ml of hydrofluoric acid, 2-3 drops of sulfuric acid, and evaporated to dryness, ignited and weighed.

A number of analyses were made for the transition metal silicides using the proposed method. For comparison, some of the samples were analyzed using the methods now in use: decomposition by fusion with soda in a platinum crucible and the separation of the silicic acid twice, fusion with sodium peroxide in nickel crucibles also with the double separation of the silicic acid, sintering with a mixture of soda and zinc oxide (Table 2). It follows from the data that the suggested method is as good in terms of its accuracy as the known methods and gives a savings in time because of the single separation of the silicic acid.

TABLE 2
DETERMINATION OF SILICON IN SILICIDES, %

Silicide	Fusion with sodium peroxide and double separation of silicic acid	Fusion with soda with the double separation of silicic acid	Fusion w/a. mixture of zinc oxide and soda w/ a single separation of silicic acid	Deviation from the average value	Mean Square error for the method
HSi ₂	25,2	25,1	25,0 25,2 24,8 25,5	-0,1 +0,1 -0,3 +0,4	$2,25 \cdot 10^{-2}$
ZrSi ₂	34,4	34,2	34,4 34,5 34,3	+0,1 -0,1 0	$0,33 \cdot 10^{-2}$
VSi ₂	48,6	48,5	48,7 48,9 48,3	+0,1 +0,3 -0,3	$3,16 \cdot 10^{-2}$
CrSi ₂	48,6	48,4	48,5 48,8 48,6	-0,1 +0,2 0	$0,83 \cdot 10^{-2}$

CONCLUSIONS

1. A method of sintering with a mixture of zinc oxide and anhydrous sodium carbonate in nickel crucibles is proposed for the decomposition of the silicides of the Group IV-VI transition elements.

2. A reasonable method has been developed for determining the total silicon concentration in the silicides of the Group IV-VI transition elements by the sulfuric acid method with a single separation of the silicic acid.

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/160

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